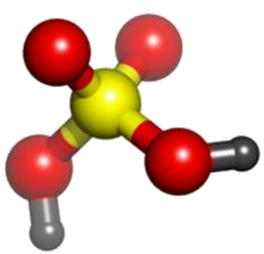
Personal Protective Equipment



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Personal Protective Equipment (PPE)

- Limitations of PPE
- Hazard assessment
- Training
- Characteristics of PPE
- Protective clothing
- Gloves
- Eyewear
- Respirators
- Exercise

Limitations of PPE

- The least desirable control, but may be necessary if:
  - Engineering controls are being installed
  - Emergency response/spill cleanup
  - Non-routine equipment maintenance
  - To supplement other control methods
- Problems with PPE:
  - The hazard is still present with PPE
  - Use is very dependent on human behavior
  - Proper fitting is essential
- Can exposure be controlled by other means?

PPE Hazard Assessment

- Identify the hazard(s)
  - Chemical
  - Mechanical
  - Electrical
  - Light energy (lasers, welding)
  - Fire response
  - Hot processes
- Identify the potential exposure route
  - Inhalation
  - Skin contact
  - Eye contact

PPE Hazard Assessment

- Identify the type of skin contact
  - Immersion
  - Spray
  - Splash
  - Mist
  - Vapor (gaseous)
- Consider the exposure time
  - Incidental contact
  - Continuous immersion
  - Unknown/emergency response

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Exercise

- List one work activity in your laboratory that uses PPE
- What is the hazard?
- What is the route of exposure? Inhalation, skin, eyes, or ?
- Are there ways to control exposure to this hazard other than PPE?
- What other ways?

Training

Employees should be trained to know:

- When PPE is necessary
- What PPE is necessary
- How to properly don, doff, adjust and wear PPE
- Limitations of PPE
- Proper care, maintenance, useful life and disposal
- Involve workers in selection

http://www.free-training.com/OSHA/ppe/Ppemenu.htm

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Training

Retraining is necessary when there is:

- A change in the hazards
- A change in the PPE required
- Inadequate worker knowledge or use of PPE

http://www.free-training.com/OSHA/ppe/Ppemenu.htm

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General Characteristics of PPE

Protective clothing and gloves:

- Act as a barrier to prevent contact with the skin

- Protect against
  - Toxics
  - Corrosives
  - Irritants
  - Sensitizers (allergens)
  - Thermal injury (burns)
  - Physical Trauma

General Characteristics of PPE

<u>Protective clothing and gloves</u>

- When selecting consider:
  - Permeation
    - Breakthrough time
    - ASTM F739 Standard
  - Penetration
  - Degradation
  - Comfort
  - Heat stress
  - Ergonomics
  - Cost

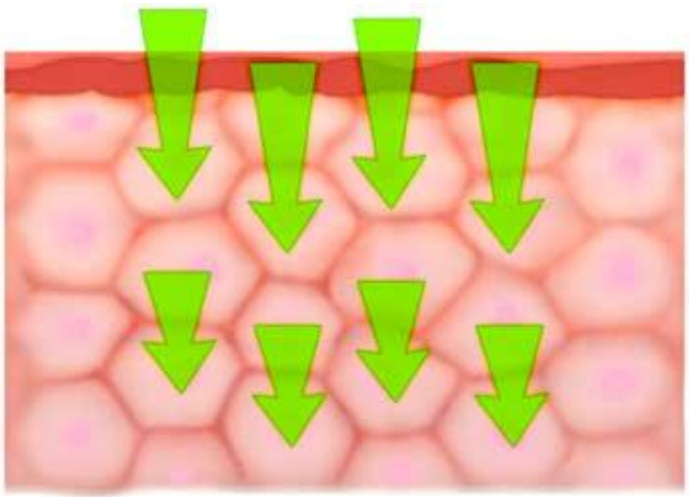

Photo credit: Permeation, http://www.cdc.gov/niosh/topics/skin/

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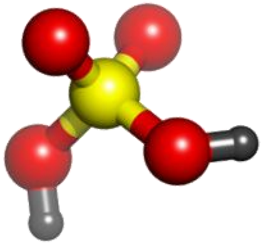
Permeation Rate (PR)	Permeation Breakthrough (PB)	Permeation Degradation rate (DR)
E- Excellent; permeation rate of less than 0.9 $mg/cm^2/min$	>Greater than (time - minutes)	E - Excellent; fluid has very little degrading effect.
VG - Very Good; permeation rate of less than 9 $mg/cm^2/min$	< Less than (time - minutes)	G - Good; fluid has minor degrading effect.
G - Good; permeation rate of less than 90 $mg/cm^2/min$		F - Fair; fluid has moderate degrading effect.
F - Fair; permeation rate of less than 900 $mg/cm^2/min$		P - Poor; fluid has pronounced degrading effect.
P - Poor; permeation rate of less than 9000 $mg/cm^2/min$		NR - Fluid is not recommended with this material.
NR - Not recommended; permeation rate greater than 9000 $mg/cm^2/min$		† Not tested, but breakthrough time > 480 min DR expected to be Good to Excellent
		†† Not tested, but expected to be Good to Excellent based on similar tested materials

Protective Clothing

- Special Applications
  - Hot processes
  - High voltage/arc flash
    - NFPA 70E
  - Foundries/molten metal
  - Refineries
- Select flame resistant clothing
- Chemical resistant coating may be added to flame resistant clothing



Gloves

- **Evaluate the work task**
  - **Chemical immersion or incidental contact?**
  - **Consider ergonomics/dexterity required**
- **Use glove charts**
  - **Charts recommend gloves for specific chemicals**
    - **Evaluate permeation rates and breakthrough time of selected glove for the specific task**
  - **Consider several glove manufactures data before final selection.**
    - http://www.mapaglove.com
    - http://www.ansellpro.com
    - http://www.bestglove.com/site/chemrest/

The first square in each column for each glove type is color coded. This is an easy-to-read indication of how we rate this type of glove in relation to its applicability for each chemical listed. The color represents an overall rating for both degradation and permeation. The letter in each square is for Degradation alone…

- GREEN: The glove is very well suited for application with that chemical.
- YELLOW: The glove is suitable for that application under careful control of its use.
- RED: Avoid use of the glove with this chemical.

CHEMICAL	LAMINATE FILM BARRIER			NITRILE SOL-VEX			UNSUPPORTED NEOPRENE 29-865			SUPPORTED POLYVINYL ALCOHOL PVA			POLYVINYL CHLORIDE (Vinyl) SNORKEL			NATURAL RUBBER CANNERS AND HANDLERS*			NEOPRENE/ NATURAL RUBBER BLEND CHEMI-PRO*		
	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate
1. Acetaldehyde	■	380	E	P	—	—	E	10	F	NR	—	—	NR	—	—	E	7	F	E	10	F
2. Acetic Acid	■	150	—	G	270	—	E	60	—	NR	—	—	F	180	—	E	110	—	E	260	—
3. Acetone	▲	>480	E	NR	—	—	E	10	F	P	—	—	NR	—	—	E	10	F	G	10	G
4. Acetonitrile	▲	>480	E	F	30	F	E	20	G	■	150	G	NR	—	—	E	4	VG	E	10	VG
5. Acrylic Acid	—	—	—	G	120	—	E	390	—	NR	—	—	NR	—	—	E	80	—	E	65	—
6. Acrylonitrile	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
7. Allyl Alcohol	▲	>480	E	F	140	F	E	140	VG	P	—	—	P	60	G	E	>10	VG	E	20	VG
8. Ammonia Gas	■	19	E	▲	>480	—	▲	>480	—	—	—	—	■	6	VG	—	—	—	■	27	VG
9. Ammonium Fluoride, 40%	—	—	—	E	>360	—	E	>480	—	NR	—	—	E	>360	—	E	>360	—	E	>360	—
10. Ammonium Hydroxide	E	30	—	E	>360	—	E	250	—	NR	—	—	E	240	—	E	90	—	E	240	—
11. Amyl Acetate	▲	>480	E	E	60	G	NR	—	—	G	>360	E	P	—	—	NR	—	—	P	—	—
12. Amyl Alcohol	—	—	—	E	30	E	E	290	VG	G	180	G	G	12	E	E	25	VG	E	45	VG
13. Aniline	▲	>480	E	NR	—	—	E	100	P	F	>360	E	F	180	VG	E	25	VG	E	50	G
14. Aqua Regia	—	—	—	F	>360	—	G	>480	—	NR	—	—	G	120	—	NR	—	—	G	180	—
15. Benzaldehyde	▲	>480	E	NR	—	—	NR	—	—	G	>360	E	NR	—	—	G	10	VG	G	25	F
16. Benzene, Benzol	▲	>480	E	P	—	—	NR	—	—	E	>360	E	NR	—	—	NR	—	—	NR	—	—
17. Benzotrichloride	—	—	—	E	>480	E	NR	—	—	—	—	—	—	—	—	NR	—	—	NR	—	—
18. Benzotrifluoride	—	—	—	E	170	G	F	—	—	E	—	—	G	<10	F	P	50	G	—	—	—
19. Bromine Water	—	—	—	E	>480	E	E	>480	E	—	—	—	—	—	—	—	—	—	—	—	—
20. 1-Bromopropane	▲	>480	E	■	23	F	■	<10	P	▲	>480	E	■	<10	F	■	<10	P	■	<10	P

General Types of Glove Material

Laminated Gloves: 4H®, Silver Shield®

- Useful for a wide range of chemicals.

  <u>Not Hydrogen Fluoride!</u>

- Can use with a nitrile over glove to improve dexterity.

Butyl Rubber

- Highest permeation resistance to gas or water vapors.
- Uses: acids, formaldehyde, phenol, alcohols.

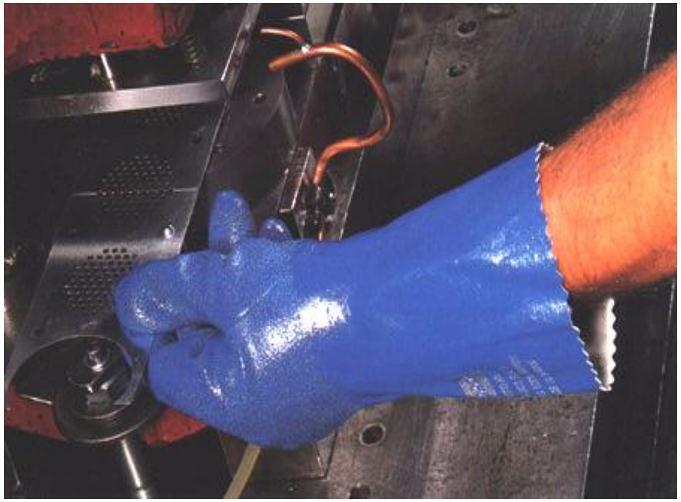
General Types of Glove Material

Neoprene

- Protects against acids, caustics.
- Resists alcohols, glycols.

Nitrile

- Good replacement for latex
- Protects against acids, bases, oils, aliphatic hydrocarbon solvents and esters, grease, fats
- NOT ketones
- Resists cuts, snags, punctures and abrasions



Latex Allergy

Proper Steps for Removing Gloves


1


2


3


4


5


6

Eye and Face Protection

- Each day, 2000 U.S. workers have a job-related eye injury that requires medical treatment.
- Nearly *three out of five* U.S. workers are injured while failing to wear eye and face protection.

NIOSH. (2010). http://www.cdc.gov/niosh/topics/eye/

Types of Eye Hazards

Hazard Type	Common related tasks	Protective Eyewear
Impact	Chipping, grinding, machining, abrasive blasting, sawing, drilling, riveting, sanding,…	Safety glasses with sideshields Goggles
Heat	Furnace operations, smelting, pouring, casting, hot dipping, welding, …	Face shield with infrared protection
Chemicals	Pouring, spraying, transferring, dipping acids, solvents or other injurious chemicals	Goggles Faceshield
Particles/ Dust	Woodworking, metal working, and general dusty conditions	Safety glasses with sideshields
Optical Radiation	Welding, torch-cutting, brazing, and laser work	Welding helmet Laser glasses -Must protect for specific wavelength of ultraviolet or infrared radiation.

Examples of Eye & Face Protection


- Goggles
- Face shield
- Safety glasses
- Welding helmet
- Hooded faceshield



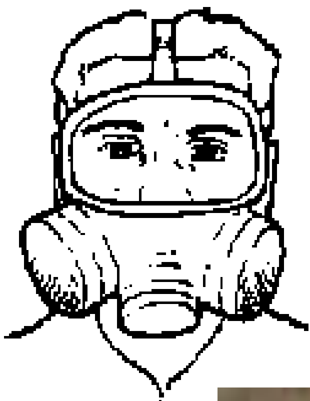
Respiratory Protection

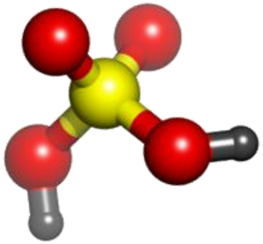
U.S. Respirator Requirements

- Written program
- Hazard assessment
    - Air monitoring
- Medical clearance
- Fit testing
- Respirator selection
- Procedures
    - Cleaning, maintenance, repairing
- Training (annual refresher)

Basic Types of Respirators

- Air purifying (APR)
  - Half Face
  - Full Face
  - Powered APR (PAPR)
- Air supply
  - Air line
  - SCBA





Air Purifying Respirators (APR)

- Work area must have at least 19.5% oxygen
- The contaminant must have adequate warning properties. Ex. ammonia
  - Never use APR in oxygen deficient atmospheres
- APRs work by filtering, absorbing, adsorbing the contaminant or chemical reaction.
  - Filters, cartridges, canisters
- The contaminant concentration must NOT exceed the maximum use concentration.
- Some cartridges have “end of service life” indicators or can use change schedules

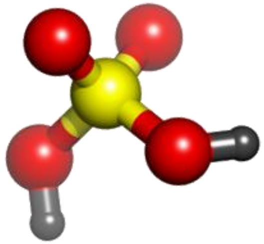
Types of APR Cartridges

Cartridge	Description
	Organic Vapor
	Organic Vapor and acid gases
	Ammonia, methylamine and P100 particulates filter

End of Service Life Indicators (ESLI)

There are very few NIOSH-approved ESLI's:

- ammonia
- carbon monoxide
- ethylene oxide
- hydrogen chloride
- hydrogen fluoride
- hydrogen sulfide
- mercury
- sulfur dioxide
- toluene-2,4-diisocyanate
- vinyl chloride



APR Filter Efficiency

National Institute of Occupational Safety and Health
Filter Efficiencies

Filter Class	
N95	Filters at least 95% of airborne particles. Not resistant to oil.
N99	Filters at least 99% of airborne particles. Not resistant to oil.
N100	Filters at least 99.97% of airborne particles. Not resistant to oil.
R95	Filters at least 95% of airborne particles. Somewhat resistant to oil.
P95	Filters at least 95% of airborne particles. Strongly resistant to oil.
P99	Filters at least 99% of airborne particles. Strongly resistant to oil.
P100	Filters at least 99.97% of airborne particles. Strongly resistant to oil

Assigned Protection Factors (APF)

- Level of workplace respiratory protection that a respirator or class of respirators is expected to provide.
- Each specific *type* of respirator has an Assigned Protection Factor (APF).
- Select respirator based on the exposure limit of a contaminant and the level in the workplace.

Maximum Use Concentration (MUC)

= APF x Occupational Exposure Limit

(e.g. PEL, TLV)

Assigned Protection Factors

Type of Respirator	Half Face Mask	Full Facepiece	Helmet/ Hood	Loose-Fitting Facepiece
Air-Purifying	10	50	-	-
PAPR	50	1,000	25/1,000	25
Supplied-Air or Airline				
– Demand	10	50	-	-
– Continuous flow	50	1,000	25/1000	25
– Pressure demand	50	1,000	-	-
SCBA				
– Demand	10	50	50	-
– Pressure Demand	-	10,000	10,000	-

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Assigned Protection Factors

Workplace air sampling indicates the exposure to benzene is 15 parts per million (ppm). The exposure limit is 0.5 ppm (ACGIH TLV).

What respirator should you choose?

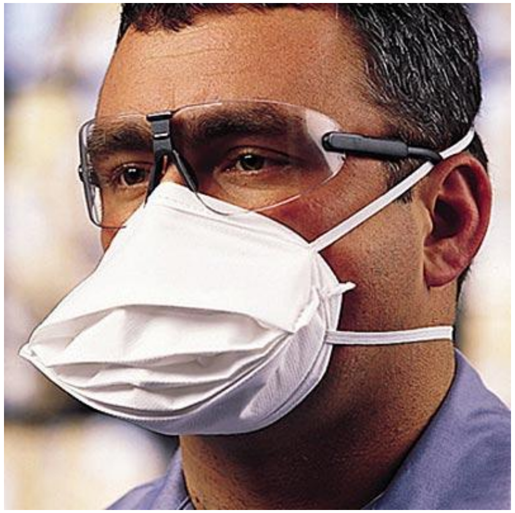
Maximum Use Concentration (MUC) = APF x OEL

Half Face Mask: MUC = 10 x 0.5 ppm = 5 ppm

PAPR (LFF): MUC = 25 x 0.5 ppm = 12.5 ppm

Full Face Respirator: MUC = 50 x 0.5 ppm = 25 ppm

Filtering Facepieces



Filtering Facepiece Use

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Respirator Fit Testing

- Qualitative
  - Irritant smoke
    - stannic chloride
  - Isoamyl acetate
    - banana oil
  - Saccharin
  - Bitrex
- Quantitative
  - Portacount

Respirator Fit Test

Positive / Negative pressure fit test

Supplied Air

- Supplies breathing air to worker
  - SCBA
  - Airline
- Must use Grade D Air
- Many limitations

Breathing Air Quality and Use

- Compressed breathing air must be at least Type 1 - Grade D [ANSI/CGA G-7.1-1989]:
  - Oxygen content = 19.5 - 23.5%
  - Hydrocarbon (condensed) = 5 milligrams/cubic meter or less
  - CO $\leq$ 10 parts per million (ppm) or less
  - CO_2 of 1,000 parts per million (ppm) or less
  - Lack of noticeable odor
- Compressors may be equipped with in-line air-purifying sorbent beds and filters.

Maintenance & Storage Procedures

- Disposable filtering face-piece:
  - Dispose after use
- Air purifying respirators:
  - Discard cartridges based on expiration date, end-of-service life indicator or calculated service life
  - Clean
  - Dry
  - Place in sealable bag (write your name on bag)
  - Contact Safety Office for repairs
- SCBA:
  - Inspected monthly
  - Accessible and clearly marked

Discussion

- A contractor has been hired to sweep out a work area that contains lead dust. The plant safety officer has recommended that the worker don a full-face air purifying respirator with a HEPA filter (P100) during this activity.
- Later that week the plant safety officer observes the worker sweeping without wearing the respirator. When asked why he is not wearing the respirator, the worker states “it is too uncomfortable to wear.”
- What approach should the safety officer take to ensure the worker wears a respirator?

PPE Exercise

- Worker A needs to transfer 10 liters of acetone into a hazardous waste drum.
- The safety officer has determined that due to the use of ventilation, the air concentration of acetone is below the exposure limit.
- The worker may have incidental skin contact with the acetone during pouring.
- Prolonged skin exposure to acetone causes dry and cracked skin, but acetone is not normally absorbed through the skin.
- There is also a possibility that the acetone may splash in the worker's face during pouring.

What PPE should Worker A wear?

PPE Exercise

- Worker B is walking back from the break room when he notices a yellow cloud of chlorine coming towards him from the chlorine storage area. He also notices that some of the chlorine has come into contact with water under one of the tanks and formed chlorine hydrate.
- He alerts the emergency response team who arrive at the emergency staging area.
  - Chlorine is a corrosive and toxic gas by inhalation.
  - Chlorine hydrate is corrosive to the skin and eyes.
  - The airborne concentration of chlorine is unknown in this situation.

What PPE should the emergency response team use?

PPE Exercise

- Worker C is tasked with adding zinc oxide pigment into a mixing bath by hand.
- This task will take 15 minutes.
- Worker C performs this task once every day.
- The safety officer has determined that the airborne concentration during this task is <u>20 milligrams/cubic meter</u>.
- The short term exposure limit (15 minutes) for zinc oxide is <u>10 milligrams/cubic meter</u> .
- Zinc oxide powder is mildly irritating to the skin and eyes, but not toxic or corrosive.

<u>What PPE should Worker C wear?</u>

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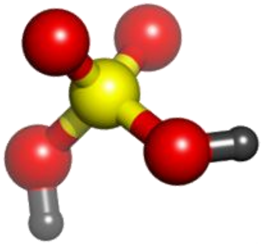
Summary

- Be Aware of the limitations of PPE and under what circumstances it can and cannot be used.
- Perform a complete hazard assessment, knowing what chemicals are present and in what state they exist in the work environment. Account for emergency situations.
- Ensure that all individuals who may use PPE in a hazardous environment are properly trained in the usage and maintenance of PPE. Include PPE training records and course materials as part of your chemical management program.
- Understand the characteristics of the PPE you intend to use. Materials, configuration and coverage of the equipment are all factors to consider.

Summary

- Protective clothing; consider what the employee is exposed to, how much are they exposed to and what type of environment they will be working in.
- When using gloves choose the correct glove materials for the chemicals you anticipate coming in contact with.
- Respirators should only be issued to trained users. Beware asphyxiating environments when using air purifying respirators.



Chemical Management

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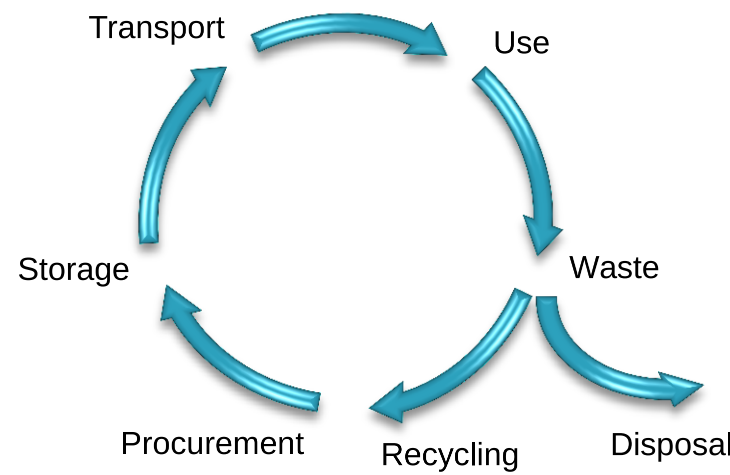
Sandia National Laboratories

Module Overview: Chemical Management

- Module Learning Outcomes
- Key Principles
- Activity: Chemical Management Best Practices
- Procurement
- Inventory Management
- Storage
- Transport
- Use of Chemicals
- Waste Management
- Activity: Chemical Management Assessment
- Summary, Conclusions, and Evaluation



Module Learning Objectives

- Having seen the overview of this module, come up with your own learning objectives

Learning	Metric	Future Action
At end of this module, what would I like to have learned?	How will I know when I have learned it?	How will I use this new learning after the workshop?

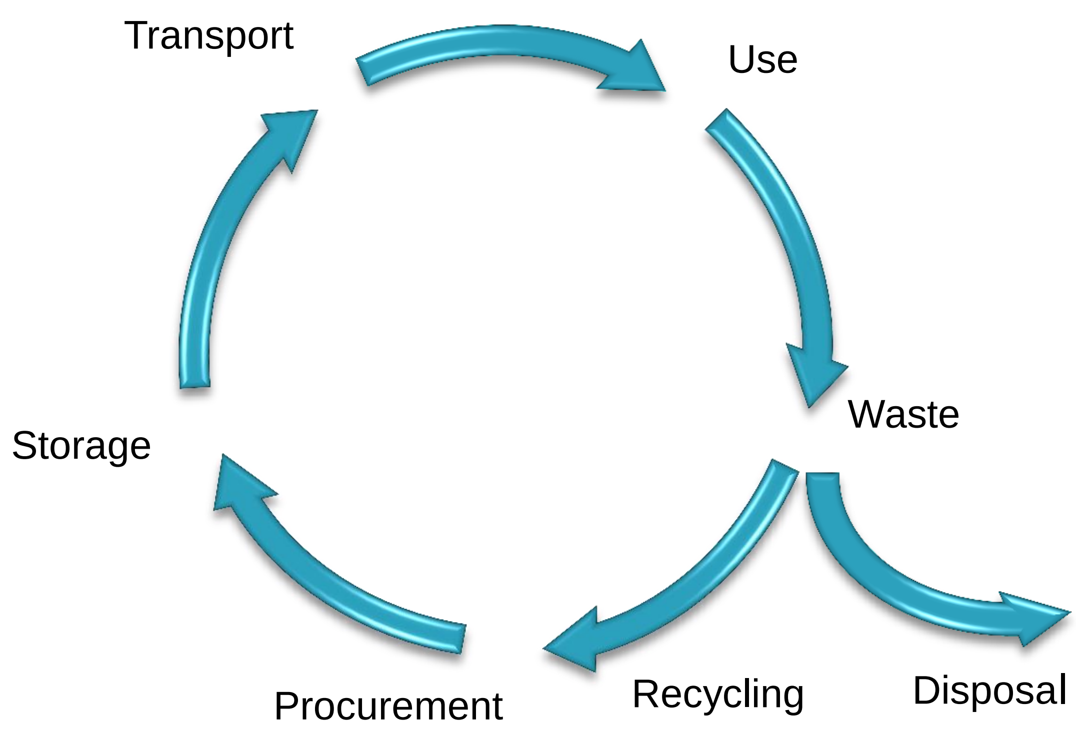
- Write your learning objectives in your worksheet in the space provided

Module Objectives: After this module, you should…

- Understand the key principles of chemical management
- Understand chemical procurement best practices
- Be able to implement safe and secure chemical storage practices
- Know the aspects of safe and secure transportation of chemicals
- Understand chemical inventory management systems
- Be able to develop a Standard Operating Procedure
- Know how to respond to chemical spills
- Understand the key elements of safe and secure chemical waste management

Key Principles: Chemical Life Cycle

- Control and accountability of chemicals at all times, from procurement to disposal as waste



Key Principles: Chemical Life Cycle

- Orphan Chemical
  - Does not have an owner
    - Person accountable
  - Does not have an apparent use or purpose
    - Surplus
  - Sometimes not labeled or identified
    - Unknown chemical

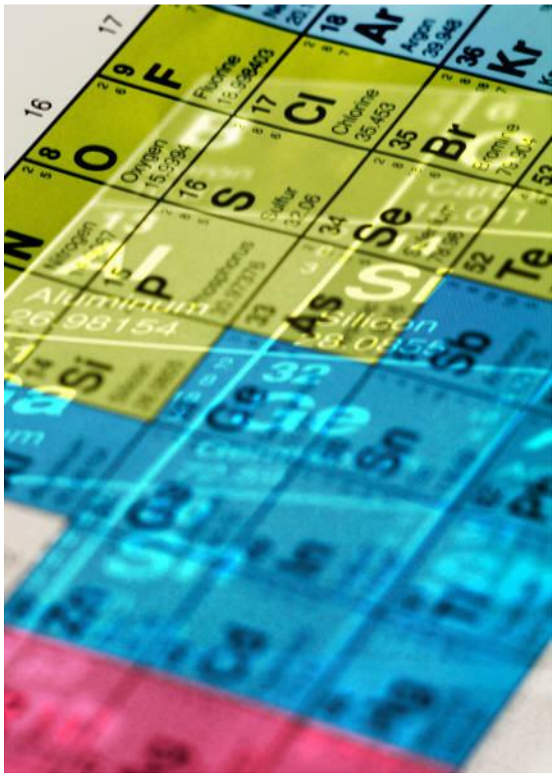
- **Cradle to Grave management of chemicals**
  - **Prevent chemicals from becoming orphans**
  - **Improve safety**
  - **Improve security**

Key Principles: Advance Planning

- When is the best time to figure out how to dispose of waste?

- Example, synthesis
  - What are the reaction products and byproducts?
    - How will they be handled?
    - How will they be stored?
    - How will they be labeled and accounted for?
    - How will they be disposed of?

Key Principles: Benefits of Chemical Management Best Practices



- Reduces Costs
- Saves Time
- Improves Research and Teaching
- Environment and Community Friendly
- Safety and Security

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Key Principles: Benefits of Chemical Management Best Practices

- Opportunities for recognition in the field of chemical management

ELSEVIER
Journal of Chemical Health and Safety
Volume 17, Issue 5, September–October 2010, Pages 13–20

Research article

An essential step for environmental protection: Towards a sound chemical management system in Malaysia

Mazlin Bin Mokhtar [Author Vitae], Goh Choo Ta [Author Vitae], Md. Wahid Murad [Author Vitae]

Available online 28 November 2009.
http://dx.doi.org/10.1016/j.jchas.2009.11.002, How to Cite or Link Using DOI

ELSEVIER
Journal of Chemical Health and Safety
Volume 18, Issue 6, November–December 2011, Pages 15–18

Feature

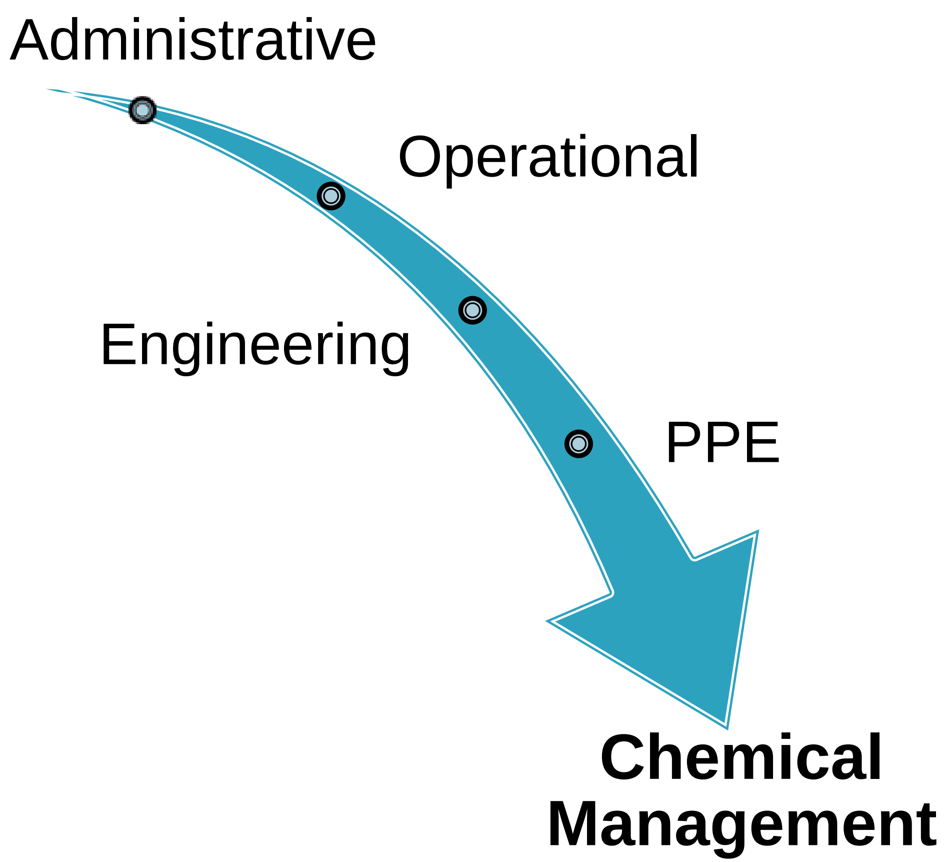
Developing a chemical and hazardous waste inventory system

Jaclyn Elizabeth R. Santos [Author Vitae], Franz Nicolas N. Alfonso [Author Vitae], Fernando C. Mendizabal Jr. [Author Vitae], Fabian M. Dayrit [Author Vitae]

Available online 12 June 2011.
http://dx.doi.org/10.1016/j.jchas.2011.05.012, How to Cite or Link Using DOI

www.sciencedirect.com

Key Principles: Components of Chemical Management



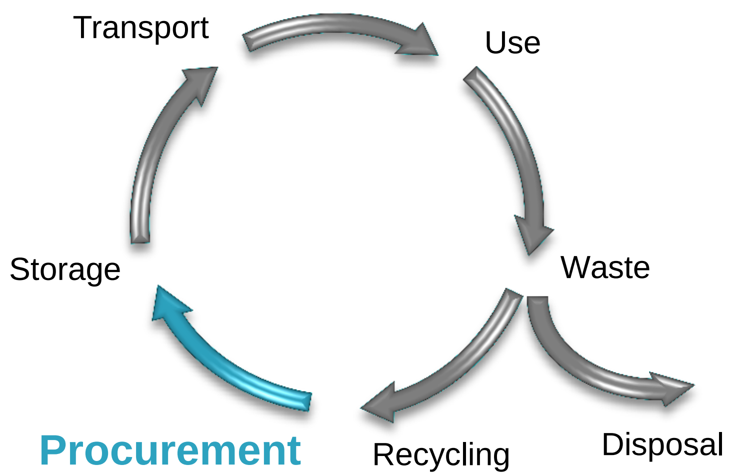
Activity: Chemical Management Best Practices

- Form groups of 3-5 people per group
- Discuss best practices for chemical management in the following areas
  - Procurement
  - Inventory management
  - Storage
  - Transport
  - Use
  - Waste
- Write down your answers and be prepared to share with the whole group

Take about 30 minutes to do this

Module Overview: Chemical Management

- ☑ Module Learning Outcomes
- ☑ Key Principles
- ☑ Activity: Chemical Management Best Practices
- **Procurement**
- Inventory Management
- Storage
- Transport
- Use of Chemicals
- Waste Management
- Activity: Chemical Management Plan
- Summary, Conclusions, and Evaluation



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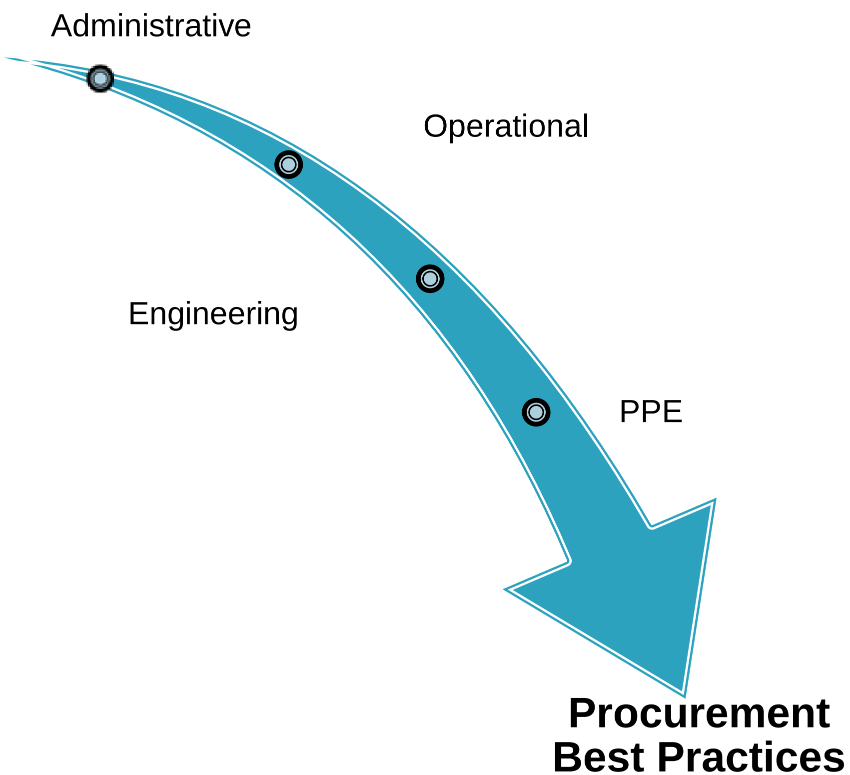
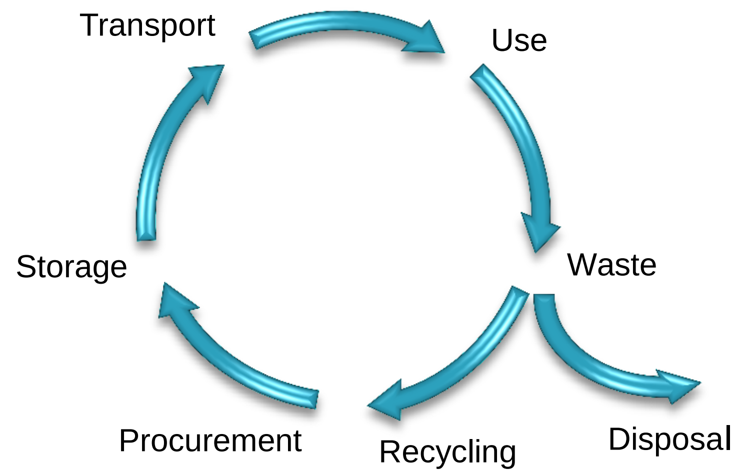
Procurement

- Planning
- Substitution
- Source reduction
- Surplus sharing
- Ordering Chemicals
- Receiving Chemicals



Procurement: Planning

- Think "Cradle to Grave" before purchasing or accepting chemicals
  - What chemicals are needed?
  - How much is needed?
  - How/where will they be stored?
  - How will they be handled/used?
  - How will disposal take place?



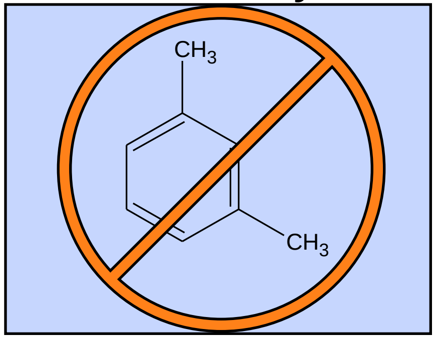
"Extra" chemicals are not usually a good idea

Donated chemicals are not always "free"

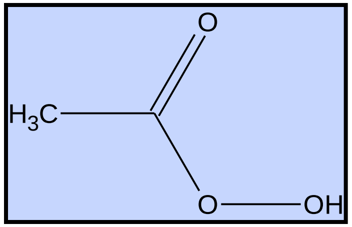
Procurement: Substitution

- Less expensive chemicals
- Less hazardous chemicals
  - Health and safety of lab personnel
  - Environment
  - Security
  - Less expensive waste disposal

- Examples:
  - Citrus-based solvents instead of xylene



  - Peracetic acid instead of formaldehyde



  - Alcohol thermometers instead of Hg

Procurement: Source Reduction

- Scale Down
  - Plan to use and purchase a smaller amount
    - Smaller cost
    - Smaller hazard
    - Easier to store
    - Easier to dispose

6th International Symposium on Microscale Chemistry, Kuwait, 2011
http://www.6ismc2011.com/images/welcome_img.jpg

Procurement: Surplus Sharing

- How it works
  - Extra chemicals in good condition are posted to a list
  - Procurement requests go first to the surplus list
  - If in stock, requester gets option of taking surplus chemicals for free
- Barriers to surplus sharing
  - Requires coordination with centralized procurement
  - Chemical collecting, hoarding
  - Requires training
- Benefits
  - Reduces cost, waste, and hazards

Procurement: Ordering Chemicals

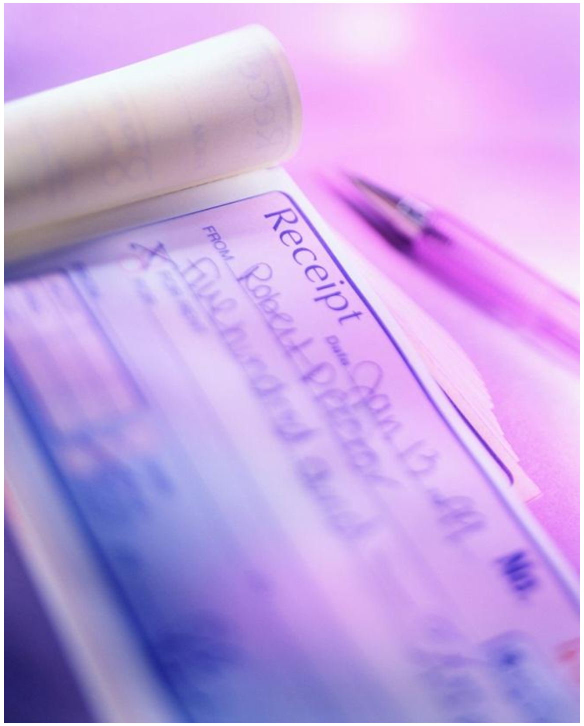
Things to Consider

- Costs
  - Purchase
  - Handling
    - Human
    - Monetary
  - Storage
  - Disposal

- Know your suppliers
  - Chemical shelf-life
    - Assay expiration, impurities
    - Hazardous decomposition
      - Peroxide-forming chemicals
  - Legitimate/licensed source

Ordering Procedure

- Centralized system
  - Ensure proper planning
  - Tracking and accountability

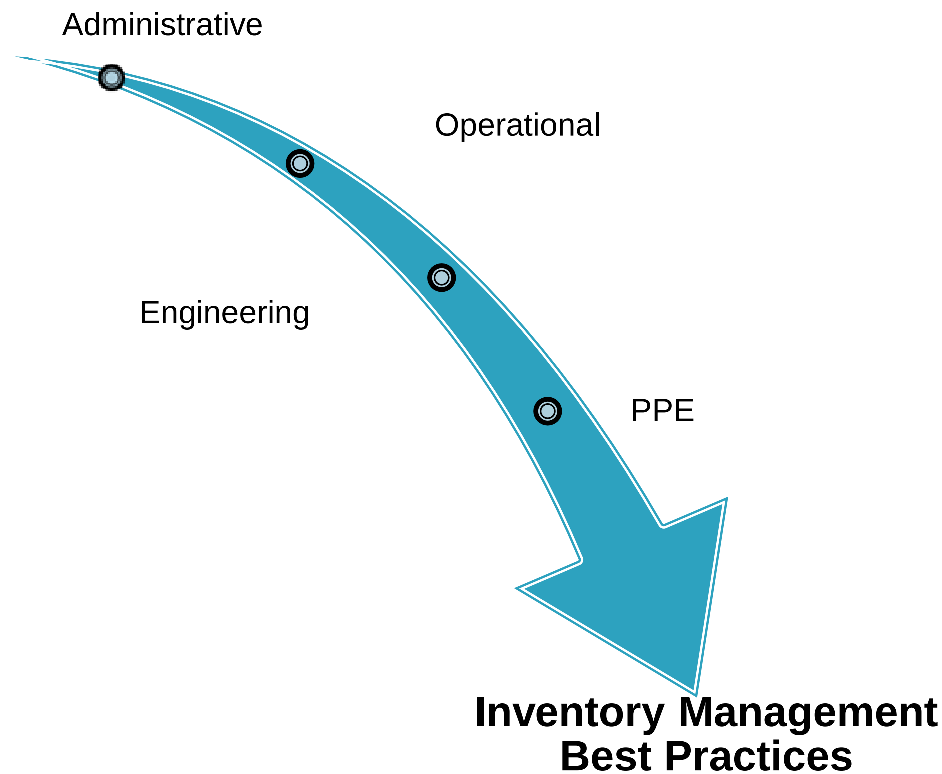


Procurement: Receiving Chemicals

- Receive deliveries of chemicals in a properly prepared area
  - Trained personnel
  - Storage requirements
  - Broken containers, spills
  - Inventory and tracking

Inventory Management

- "Living" database of chemicals
  - Updated with procurement, transport, use, and disposal
- Requires training and maintenance with inspections
- Control access to database
- Ensure control and accountability
  - Designated owner
  - No orphan chemicals
- May be required for regulatory compliance



Inventory Management

- Simple system
- Computer/web-based system
  - Barcodes
- Benefits
  - Save time
  - Save money
  - Improve research
  - Improve safety
  - Improve security
  - Regulatory compliance
  - Earn recognition
- For synthesis labs
  - Enter synthesis products into inventory or just label properly

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Inventory Management: Database

- Name
  - IUPAC, common, trade
- CAS number
- Formula
- Ingredient
- Location
  - Facility, building, room, cabinet, shelf
- Owner
  - Organization
  - Individual
- Requester
- Purchaser
- Barcode
- Supplier or producer
- Physical state
- Hazards
  - Compatibility/storage info
  - COC flag
  - Biosafety/biosecurity level
- Safety Data Sheet (SDS)
- Certificate of analysis
- Quantity
- Date purchased or received
- Expiration date
- Status (open or not)
- Use and transfer history

It is possible to keep track of a lot of useful information with a computer/web-based chemical inventory management system

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Inventory Management: Access Control

- Different levels of access to inventory system and database
  - Students
  - Faculty, staff researchers
  - Department heads, system administrators
  - Chemical safety and security officers, centralized procurement

- Outsider Threat
  - **Restrict access to information about COC locations and physical security**

- Insider threat
  - Personnel management
  - Procurement
  - **Inventory management**
    - **Chemical Owner**
    - **Physical Inspection**

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Inventory Management: Physical Inspection

- Assures accuracy of inventory database
- Provides visual assessment of chemical condition
- Should be done once or twice a year
    - More often for COCs

Inventory Management: Reporting

- Coordinate with emergency responders
- Inventory reports may be required by law or by institution policy
  - Based on location
  - Quantities of chemicals purchased or used
  - Price
  - Expiration
  - Transport
  - COCs
- Use of a computer/web-based system makes reporting easier

- 1994, California State University, Northridge
- Magnitude 6.7 earthquake, epicenter only a few km from campus
- Fires in science buildings allowed to burn because chemical inventory/hazards unknown

Image courtesy: P.W. Weigand, California State University Northridge Geology Department,
Image source: Earth Science World Image Bank http://www.earthscienceworld.org/images

Inventory Management: Examples/Demonstration

Barcode	Location	Date In	Name	Cas #	State	Quantity	Units	Container	Hazards/Alerts
AQ879816	124/2	2/12/2011	Sulfuric Acid	7664-93-9	Liquid	500	mL	Glass	acid
AQ879817	122/1	5/24/2003	Ferric Chloride	7705-08-0	Solid	500	gram	Metal Can	toxic, corrosive
AQ879818	124/3	1/1/2001	Oxygen	7782-44-7	Gas	5	m^3	Gas Cylinder	flammable
AQ879819	121/A	6/24/2005	Acetone	67-64-1	Liquid	1	L	Plastic	flammable
AQ879820	122/2	2/7/1998	Diethyl Ether	60-29-7	Liquid	1	L	Plastic	peroxide former
AQ879821	124/1	5/8/1996	Magnesium	7439-95-4	Solid	100	gram	Metal Can	flammable
AQ879823	121/B	5/30/2005	Pinacolyl Alcohol	464-07-3	Liquid	26	kg	Glass	CWC sch 2
AQ879824	121/A	10/24/2002	Sodium Cyanide	143-33-9	Solid	5	gram	Glass	toxic

- What information is missing?

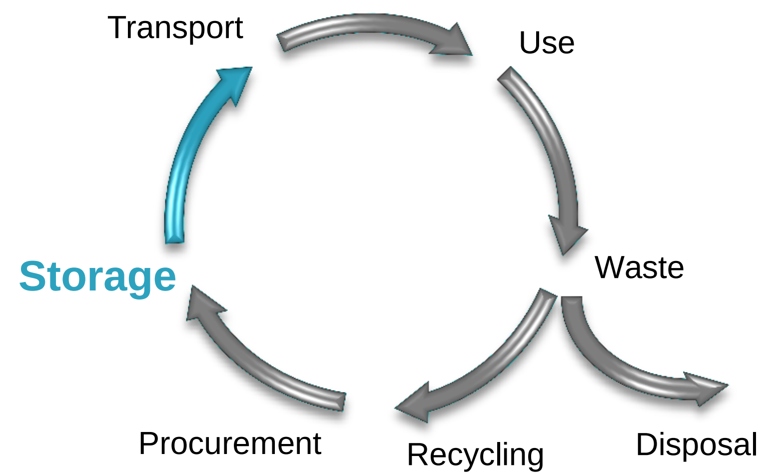
Inventory Management: Conclusions

- What are the main challenges to effective chemical inventory management?
- Benefits of a Chemical Inventory Management System
  - Save time
  - Save money
  - Improve research
  - Improve safety
  - Improve security
  - Regulatory compliance
  - Earn recognition
- Published articles about chemical inventory management[1]
  - Ateneo de Manila University
  - Stanford University
  - Temple University
  - Los Alamos National Laboratory

[1] These and other articles are in *Journal of Chemical Health and Safety* http://www.journals.elsevier.com/journal-of-chemical-health-and-safety/

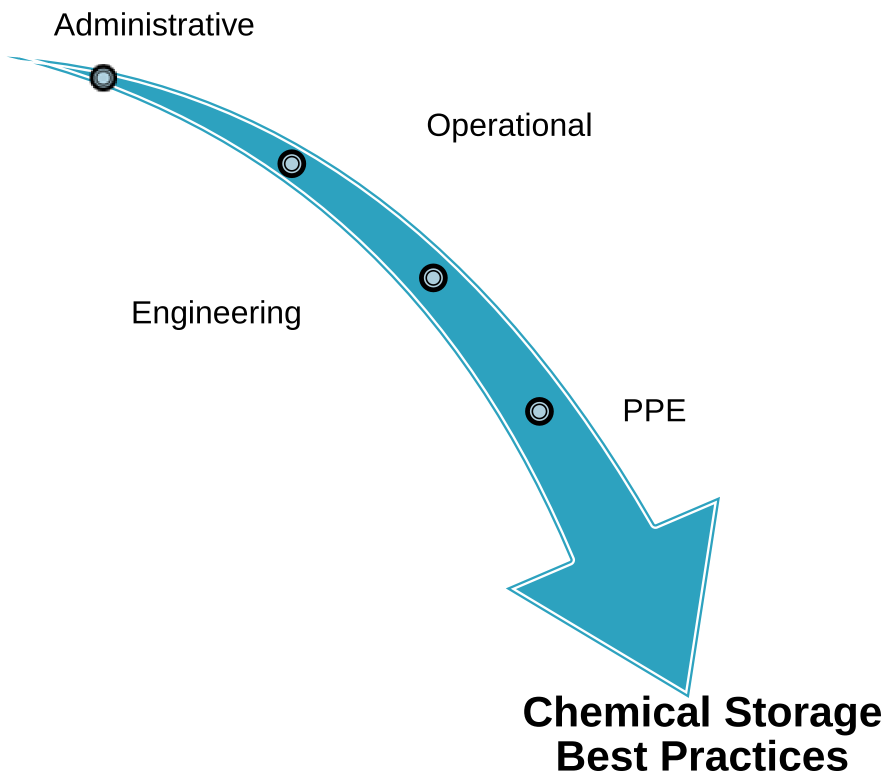
Module Overview: Chemical Management

- ☑ Module Learning Outcomes
- ☑ Key Principles
- ☑ Activity: Chemical Management Best Practices
- ☑ Procurement
- ☑ Inventory Management
- **Storage**
- Transport
- Use of Chemicals
- Waste Management
- Activity: Chemical Management Plan
- Summary, Conclusions, and Evaluation



Storage

- General Guidelines
- Reactive Chemicals
- Labels
- Compressed Gas Cylinders
- Refrigeration
- Examples
- Access Control
- Activity: Chemical Storage



Storage: General Guidelines

- Separate incompatible chemicals
- Separate flammables and explosives from ignition sources
  - Flammable storage cabinets
- Large containers on bottom shelves
- All containers properly labeled and closed

Storage: General Guidelines

- Wipe-off outside of container before returning to storage area
- Secure COCs
- Use secondary containment
  - Label with compatibility group
- Fasten storage shelves to wall or floor
- Shelves should have a lip and/or rod

Storage: General Guidelines

- **Do Not Store Chemicals**
  - On top of cabinets
  - On the floor
  - In hoods
  - Where there are wide variations in temperature, humidity or sunlight
  - In hallways
  - With food

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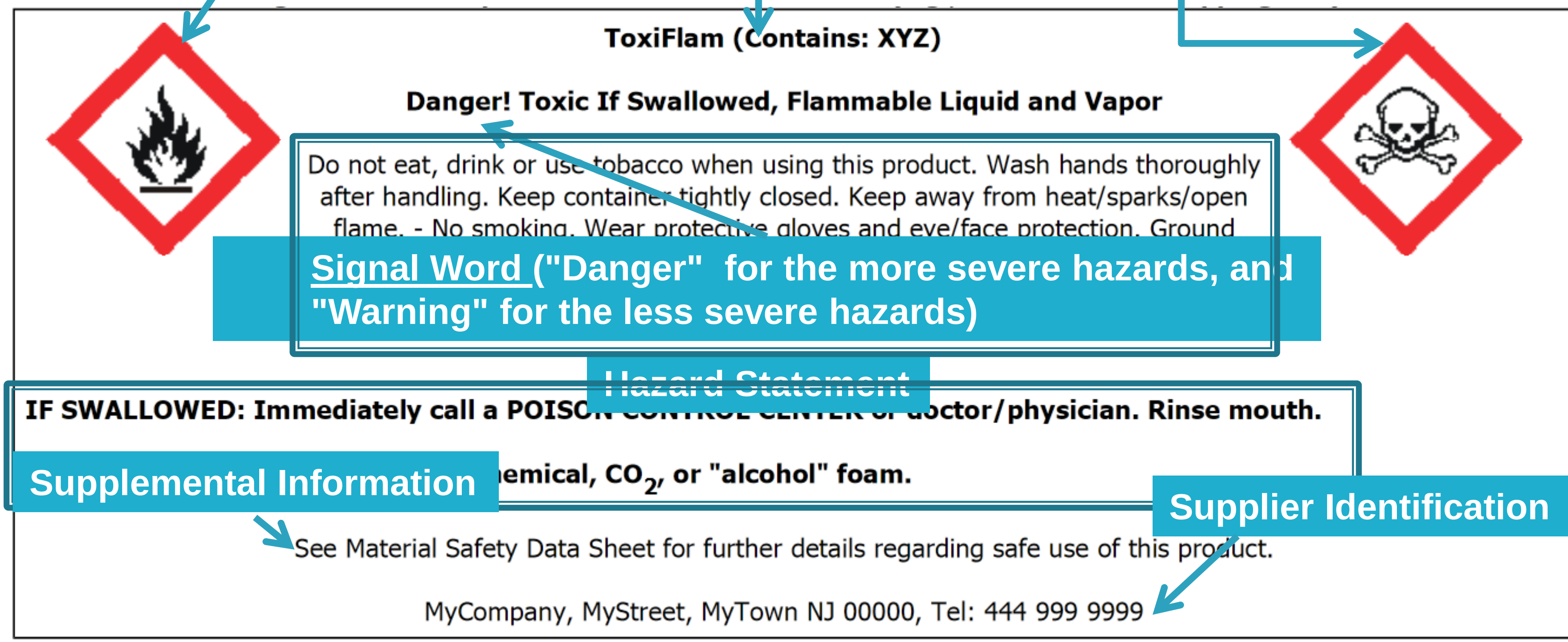
Storage: Reactive Chemicals

- Water reactive, pyrophoric, oxidizers
- Peroxide-forming
  - Ethers, butadiene, others
  - Store in tightly closed original container
  - Avoid exposure to light, air, heat
  - Crystals or discoloration? Do not move or open container
  - Test for peroxides before using
    - Especially if distilling/concentrating
  - Know when to dispose
    - Mark when opened
    - Dispose even if unused

Storage: Labels

Symbols (Hazard Pictograms)

Product Identifier and ingredient disclosure



Signal Word ("Danger" for the more severe hazards, and "Warning" for the less severe hazards)

Hazard Statement

Supplemental Information

Supplier Identification

Precautionary Statement (prevention, response in cases of accidental spillage or exposure, storage, and disposal

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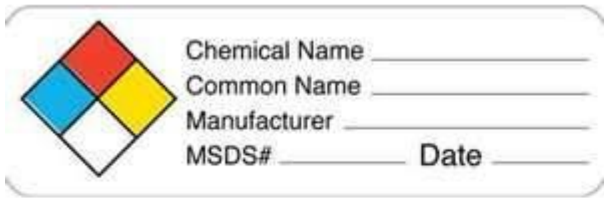
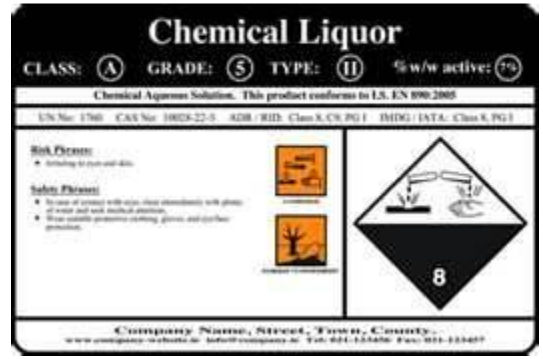
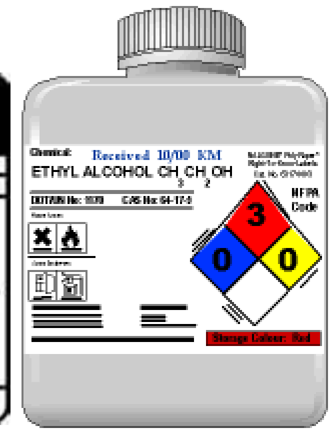
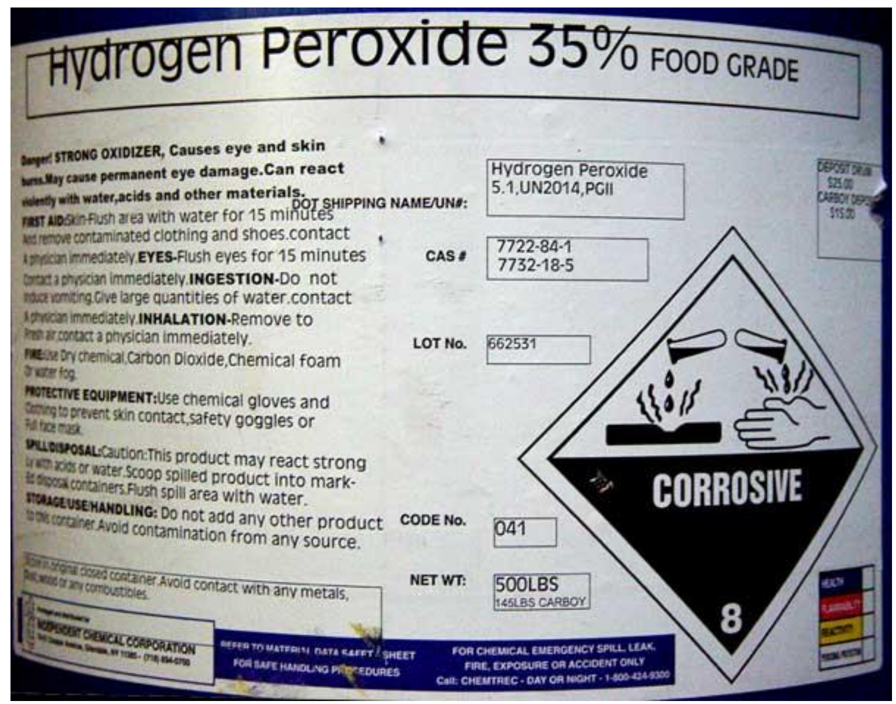
Storage: Labels









Storage: Compressed Gas Cylinders

- Keep cylinders outside and pipe into lab
- Store cylinders in lab
- Secure (chain/clamp)
- Screw down cylinder caps
- Store in well-ventilated area
- Separate and label empty cylinders
- Separate incompatible gases
- Transport safely

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Storage: Refrigeration

- Types
  - Ordinary, household refrigerator/freezers
    - **NOT safe for flammables**
  - Flammables-safe refrigerator/freezer
    - May contain flammables, but are NOT safe to be in areas with flammable vapors
  - Explosion-proof storage
- Proper refrigerator/freezer labeling
- Precautions
  - Stable power
  - Not all refrigerants are completely safe
    - Toxicity, flammability, and physical hazards
- Do not store peroxide formers in a refrigerator
- Defrost occasionally to prevent chemicals from becoming trapped in the ice formations

Storage: Examples

Storage: Access Control

- Access limitations depend on the material or information
  - More control of access if COCs are present
- Lock areas, rooms, cabinets
  - Control of keys
- Label areas "Authorized Personnel Only"
  - Means of identifying authorized personnel
- Authorized personnel
  - Trusted, background check
  - Trained
  - Legitimate need
- Chemical management
  - Inventory control and accountability

Activity: Chemical Storage

- Find one or two partners
- Use hazard and compatibility information to optimize chemical storage
- Rules:
  - 4 bottles per shelf maximum
  - Note that only one cabinet has a vent
  - Only one cabinet can be secured (padlock)

You will have to make some compromises or hard choices

- When finished, discuss the following and write comments in your workbook:
  - Was there one “perfect” way to store the chemicals?
  - What were the compromises you made? What were your priorities?

Take about 20 minutes

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Activity: Chemical Storage

Conclusions

- You can make chemical storage safer and more secure
- Safe and secure chemical storage requires
  - Space
  - Time
  - Training
  - Equipment
- Difficulties may be mitigated by operational controls
  - Substitution
  - Source reduction
- Can get help from a computer/web-based inventory system that tracks hazards and compatibilities

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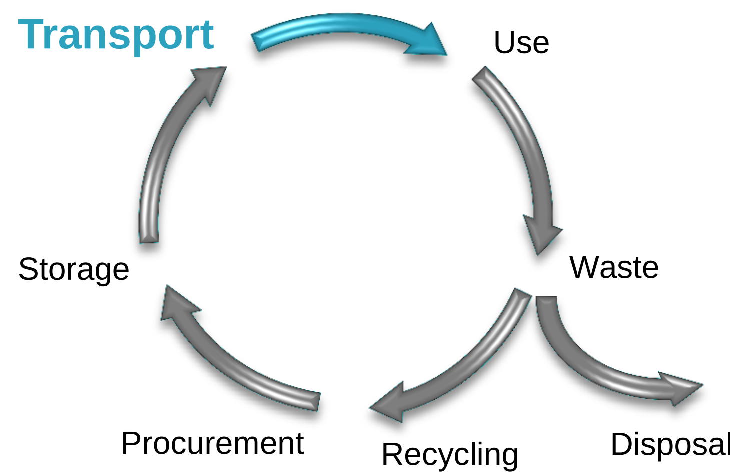
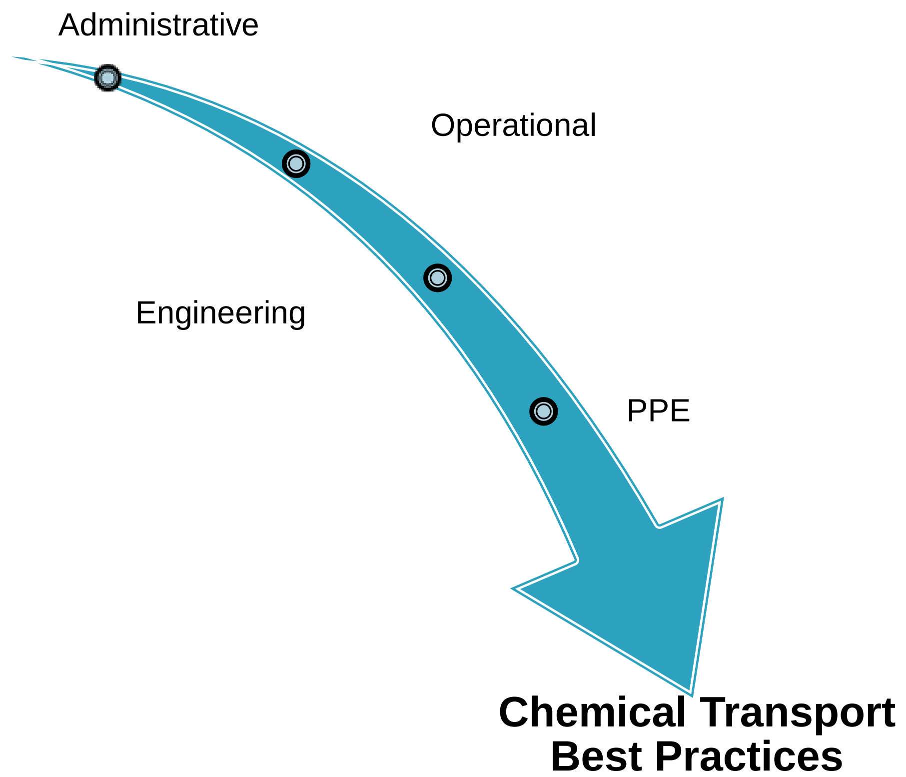


Transport

- Hazardous Shipments
- Modes of Transport
- Regulations
- Packaging
- Labels
- Documentation
- Emergencies and Security



Transportation: Hazardous Shipments

- Laboratory samples
- Equipment
- Domestic shipments
- International shipments
- Quantity of material

Take what, where, and how much into account when making hazardous shipments

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Transportation: Hazardous Shipments

- Chemical
  - Toxic
  - Oxidizers
  - Corrosive
  - Flammable
  - Explosive
- Physical
  - Cryogens
  - Compressed gases
  - Magnetic
- Biological
  - Infectious pathogens
  - Genetically modified organisms
- Radioactive substances

Take types of hazards into account when making hazardous shipments

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Transportation: Hazardous Shipments

- External events
  - Collisions, crashes, accidents
- Internal Events
  - Release or spill due to equipment or containment failure
- Consequences
  - Injuries or fatalities
  - Property damage
  - Environmental damage
  - Institution impacts
    - Fines
    - Negative press

Consider all that could go wrong and the consequences when making hazardous shipments

Transportation: Modes of Transport

- Air
- Waterway
- Rail
- Road
  - Vehicle
  - Cart or bicycle
- Hand carry
- Transport vehicle may carry both people and your shipment

Take mode of transport into account when making hazardous shipments

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Transportation: Regulations

- Thousands of regulated hazardous materials
- Differences in regulations by country
- Penalties can be severe
  - Willfully violation of US hazardous material transportation regulations
    - Fines up to $250,000
    - Prison for up to 5 years
    - Both fine and prison

- International regulations
  - UN Model Regulations
  - International Maritime Dangerous Goods (IMDG) Code
  - International Air Transport Association (IATA)
- Special requirements, restrictions, or limitations
- Training requirements, certifications

Take regulations into account when making hazardous shipments

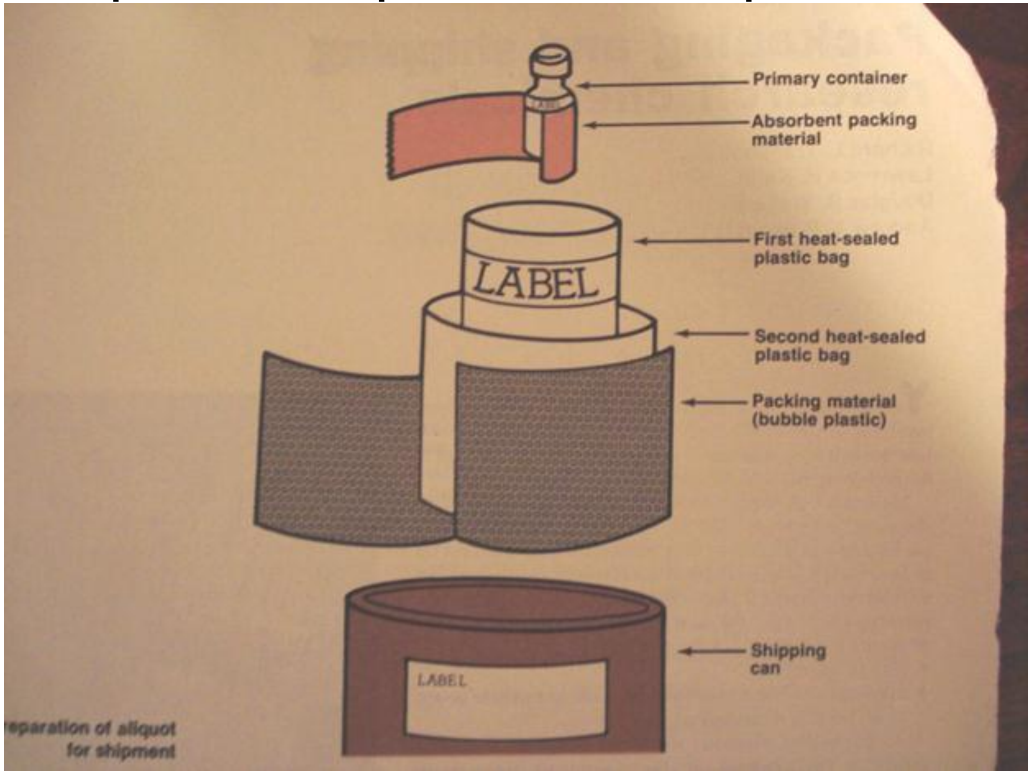
Title 18 U.S.C.
HMR; 49 CFR Parts 171-180

Transportation: Regulations

- Assistance from trained person
  - CSSO, other
  - Knows regulations
  - Has required certifications
  - Can ensure use of licensed, approved shipping companies

Transportation: Packaging

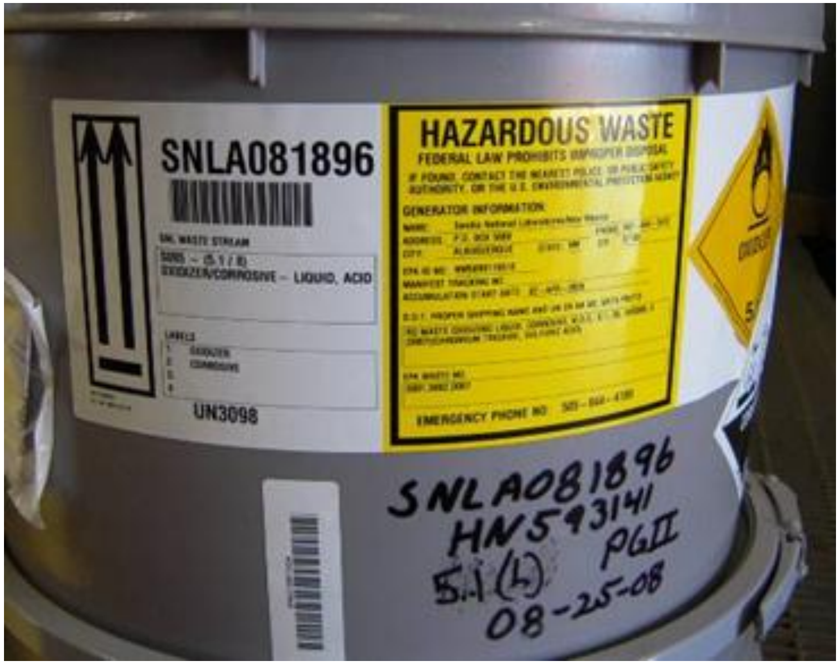
- Container within a container
- Specific requirements depend on material and other factors



Transportation: Labels

- Identify material
  - Proper, full chemical name
  - ID codes (e.g., UN number)
  - Quantities, concentrations, number of containers

- Hazard class according to regulations
  - Transport symbols
- Emergency information
- Contact names and phone numbers
- Languages



Transportation: Documentation

- Safety Data Sheets
- Shipping order
- Bill of lading
- Manifest
- Full shipper, receiver addresses
- Packing and labeling certification
- Verification of receipt

- Follow up documentation
  - Incident/accident reports

http://worldamazingpictures.files.wordpress.com/2010/09/worlds-biggest-ship-accidents-6.jpg?w=400

Transportation: Emergencies and Security

- Emergency contacts
  - Regulation requirements
    - local, national, international
- Public relations
  - Designate spokesperson beforehand
  - Be responsive to public concerns
- Higher risk shipments require higher security
  - Special regulations

Photos: TSA User's Guide on Security Seals for Domestic Cargo

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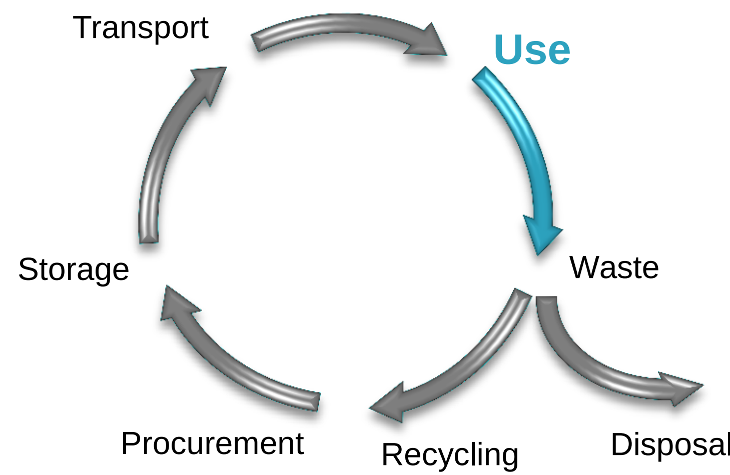

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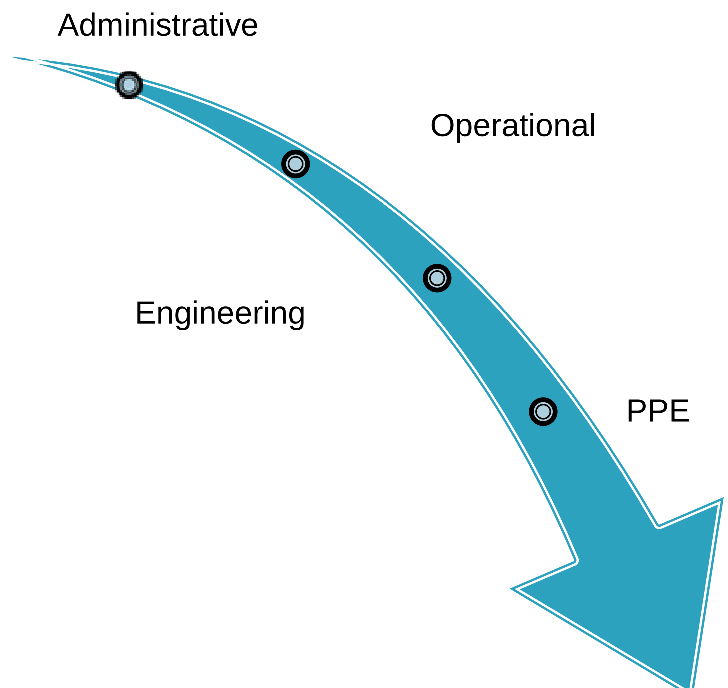
Use of Chemicals

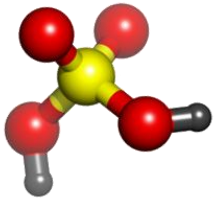
- Standard Operating Procedures (SOPs)



Best Practices for the Laboratory Use of Chemicals

- Spills

http://0.tqn.com/d/chemistry/1/7/Q/q/testtubespill.jpg



Standard Operating Procedures (SOPs)

- Describes how your lab will carry out a certain procedure

- A lab may have SOPs for
  - Security clearance and visitor access
  - Employee training
  - Respiratory protection and equipment fitting
  - Eye protection
  - Housekeeping
  - Ventilation system maintenance
  - Storage, receipt, and transport of hazardous materials
  - Accident and emergency response including natural disasters
  - Hazardous material handling or special equipment operation
    - Toxic chemicals, radiation, lasers, infectious agents, flammable chemicals
  - Spill cleanup
  - Waste management

- No specific format exists for SOPs

Standard Operating Procedures (SOPs)

- SOPs for work with hazardous chemicals can be written into a set of steps for an experiment or procedure

- Should include
  - Date
    - Issued
    - Reviewed
    - Revised
  - Subject, title and identification code
  - Amounts and/or concentrations used
  - Special handling procedures, engineering controls, and personal protective equipment
  - Official review by management, signed
  - Review by all responsible parties, signed

- Should be written in a consistent and official format
  - Example SOP templates

    http://www.safety.duke.edu/OHS/chemsopsTemplates.htm

Activity: Standard Operating Procedures (SOPs)

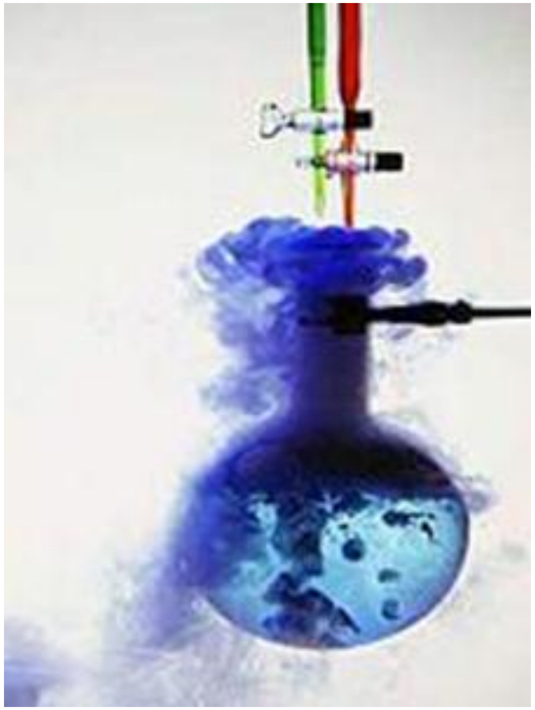
- Scenario: You are a chemist in a Quality Control (QC) lab
- Goal: Develop an SOP for preparing a standard acid solution for titration
- Get in groups of 3-5 people per group

Burette photograph courtesy of Indigo® Instruments

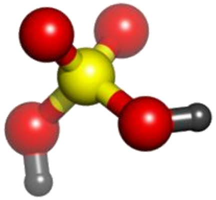
Activity: Standard Operating Procedures (SOPs)

- Refer to the SDS for H_2SO_4, and the partially completed SOP

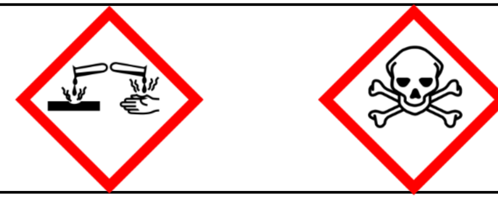
- In your groups, discuss
  - Hazards
    - Chemicals, reactions, and products
    - Equipment
    - Storage
    - Disposal
    - Security
  - Controls
    - Operational
    - Engineering
    - PPE



- Fill in the blanks to complete the SOP
  - Be prepared to discuss with the whole group



Activity: Standard Operating Procedures (SOPs)

Hazards in this SOP	
Preparation of solutions	
Equipment	
Waste/disposal	
Security	

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Activity: Standard Operating Procedures (SOPs)

<u>Controls</u>

- Operational
  - Substitution
  - Scale down
  - SOP
- Engineering
- PPE
  - Quantity dependent

Activity: Standard Operating Procedures (SOPs)

Conclusions

- SOP can be a set of steps for carrying out a laboratory task safely and securely
- Should be part of a formal training procedure
  - Update regularly
- Protects students/workers, faculty, administrators, chemicals/info

http://offthewallchemistry.blogspot.com/2011/01/chemistry-cartoons.html

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Spills: Hazard Assessment

- Plan ahead – know the worst case scenario for a spill
  - Hazards of the spilled material
    - Toxic, flammable, etc.
  - Size of spill
    - Smaller or greater than 4 L
  - Location of spill
    - Ventilation

- Know if spill is an emergency situation or not
  - Emergency
    - Isolate
    - Communicate
    - Evacuate
  - Not an emergency
    - Know the appropriate cleanup and decontamination procedures
    - Have the necessary equipment

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Spills: Preparation

- Spill Kits
  - Absorbent material
  - Neutralizing agents
    - $NaHCO_3$, citric acid powder, activa carbon (for organic solvents)
  - Plastic bucket with lid
  - Plastic dust pan
  - Broom or brush
  - Plastic bags
  - Tape
  - pH paper
  - Signs: Keep Out, Danger Chemi Spill
  - PPE for at least 2 people
    - Goggles
    - Gloves
    - Disposable aprons or jump suits
    - Disposable shoe covers
    - Respirators

- Emergency Equipment
  - Phones with emergency numbers
  - Alarms
  - Fire extinguishers
  - Emergency eyewash and showers
  - First Aid
  - Safety Data Sheets

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Spills: Prevention

- Have only the amount of chemical required
- Understand work practices and procedures
  - SOP
- Eliminate clutter
- Use secondary containers
  - Storage
  - Transport
  - Work
- Dispose of waste and excess chemicals properly and timely

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Spills: Cleanup

- Assess the hazard
- Get someone to help
- Wear appropriate PPE
- Alert people in immediate area
- Confine spill
- Absorb excess, surround area with absorbent material
  - Do not dry sweep
- Neutralize and test as necessary
- Gather contaminated absorbent material from outer edge toward center
- Collect contaminated absorbent, residues, and disposable PPE
- Clean and dry the spill area
- Restock emergency and spill kits

http://www.dawginc.com/media/catalog/category/275X275/Spill-Kits-ba.jpg

Spills: Reporting

- Maintain accurate records of near misses, incidents, and response
  - All involved personnel
  - Exposure measurements
  - Medical treatment
- Examine records for patterns
  - Use to improve safety and security program
- Encourage reporting and discourage hiding of incidents
  - Maintain confidentiality

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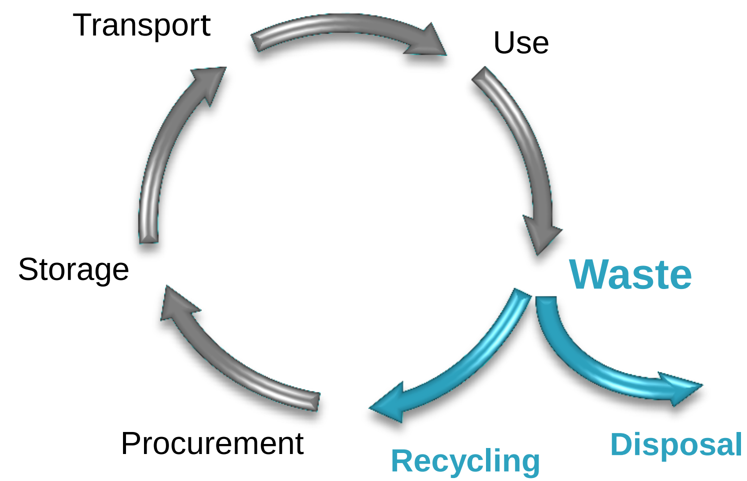
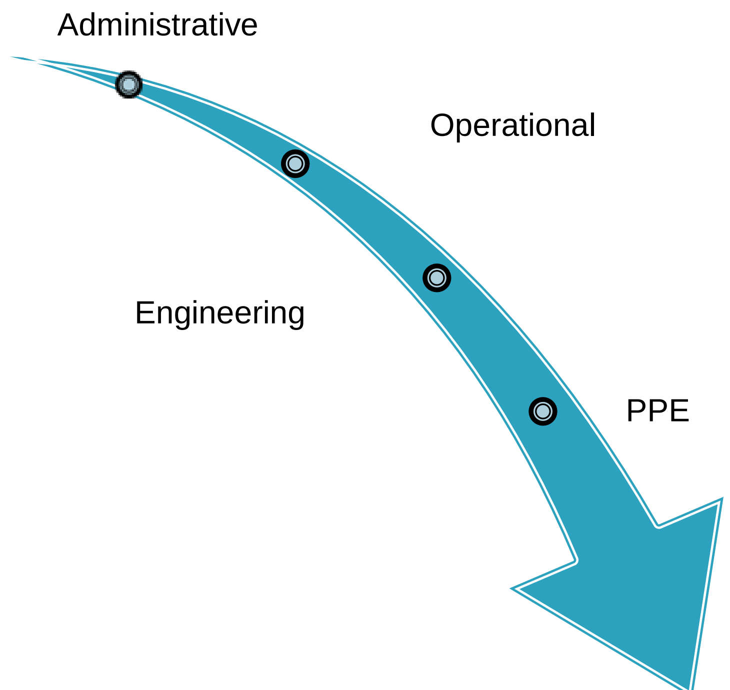
Module Overview: Chemical Management

- ☑ Module Learning Outcomes
- ☑ Key Principles
- ☑ Activity: Chemical Management Best Practices
- ☑ Procurement
- ☑ Inventory Management
- ☑ Storage
- ☑ Transport
- ☑ Use of Chemicals
- **Waste Management**
- Activity: Chemical Management Plan
- Summary, Conclusions, and Evaluation



Waste

- Prevention
- Categories
- Treatment
- Collection
- Activity: Waste Container Label
- Storage
- Recycling
- Disposal
- Orphans and Unknowns



Best Practices for Waste Recycling and Disposal

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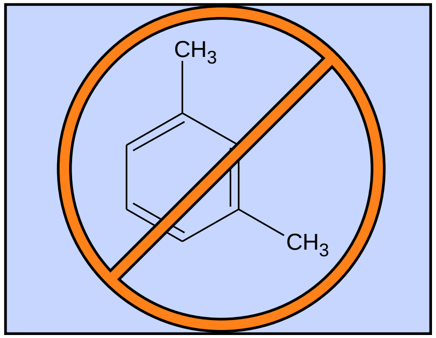
Waste: Prevention

- Substitution
  - Replace a hazardous chemical with a less hazardous one



- Source Reduction
  - Scale down
  - Procure and use less

6th International Symposium on Microscale Chemistry, Kuwait, 2011
http://www.6ismc2011.com/images/welcome_img.jpg

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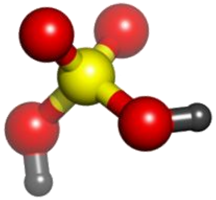
Waste: Categories

- Nonhazardous Waste (if uncontaminated)
  - Used oil
  - PPE
  - Some salts, sugars, amino acids
  - Some resins, gels, sand, etc.

- Hazardous Waste
  - Toxic, flammable, etc.

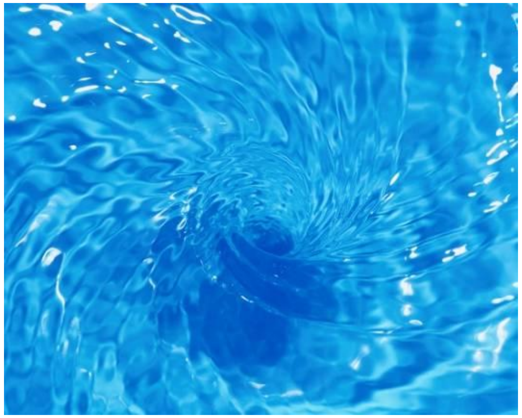
- Hazardous Mixed Waste
  - Chemical
  - Biological
  - Radiological



Waste: Treatment

For Disposal - Not legal everywhere

- If legal, deactivate/neutralize and dispose of some wastes in the lab yourself
  - Example: Acids and Bases
    - Do not damage drain pipes
    - Dilute with lots of water while pouring down the drain
    - Be sure not to form more hazardous substances
    - Check references, scientific literature



Waste: Treatment

If legal, consider treating waste to reduce the volume

- Evaporation
  - Only if can be done safely
    - Not with corrosive, radioactive, peroxides or peroxide-formers
- Adsorption
  - Activated carbon
  - Activated alumina
  - Ion exchange
- Precipitation - Extraction

Minimization of the volume of waste is best accomplished when?

http://www.sartorius.com/typo3temp/pics/LT_Vivapure-_0430_RGB_ca7cec6815.jpg

Waste: Treatment

If legal, consider treating waste to reduce the hazards

- Requires chemical expertise
  - Ability and legality may be specific to each chemical
- Dilution
  - H_2O_2, $HClO_4$, HNO_3
    - Never add water to a concentrated acid
- Hydrolysis
  - Halogen compounds with NaOH
  - Carboxamides with HCl
- Oxidation - Reduction

Minimization hazards of waste is best accomplished when?

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Waste: Treatment

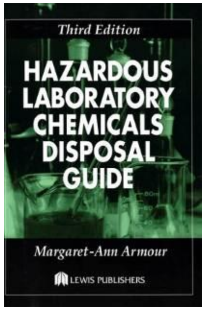
References

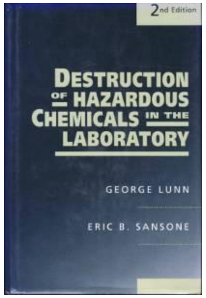
- “Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 8.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 2011, available online: http://dels.nas.edu/Report/Prudent-Practices-Laboratory-Handling/12654

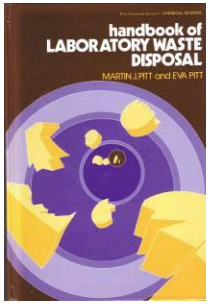
- “Destruction of Hazardous Chemicals in the Laboratory, 2nd Edition”, George Lunn and Eric B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999

- “Hazardous Laboratory Chemicals Disposal Guide, Third Edition”, Margaret-Ann Armour, CRC Press, 2003, ISBN 978-1566705677

- “Handbook of Laboratory Waste Disposal”, Martin Pitt and Eva Pitt, 1986, ISBN 0-85312-634-8







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Waste: Collection Areas

- Create safe and secure waste collection areas
- Example, waste collection area in teaching/research labs
  - Convenient student use
  - Emptied/moved frequently
  - Divided into chemically compatible groups
  - Provide safety equipment

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Waste: Collection Containers

- Avoid creating mixed waste during collection
- Use separate containers for incompatible wastes (e.g., organic solvents and oxidizers)

- Container must be compatible with waste (e.g., no hydrofluoric acid in glass)
- Label containers

- Keep containers closed
- Use secondary containment
- Avoid using containers that will easily break

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Waste: Storage

- Use the same safety and security precautions for waste storage area that are used in the laboratory
  - Access control
  - Warning signs
  - Storage considerations
  - Ventilation
  - Emergency equipment
  - Spill kits
  - PPE
- Facility should be designed and prepared for spills/chemical releases on a larger scale
  - Leak collection, containment, cleanup

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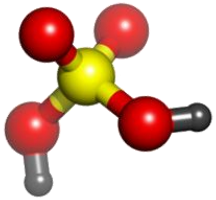
Waste: Storage

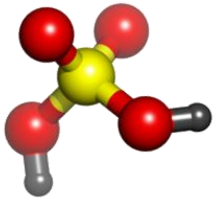
- Small containers of compatible waste
- Packed in absorbent materials
- Labeled
- Separated
- Secured



Waste: Recycling

- Reuse by others in the organization or community
- An active chemical exchange program
- Beware of accepting unusable chemicals
- Reuse in experiments in the laboratory
- Exchange for credit with suppliers by agreement
- Build recycling into curriculum
  - Using waste to test an analytical method
  - Waste remediation research

Donated chemicals are not always "free"



Waste: Recycling

<u>May Recycle (examples)</u>

- Excess unopened chemicals
- Excess laboratory glassware (unused or clean)
- Consumables with no expiration
- Some precious or toxic me
  - Hg, Ag, Pt, Pd, Au, Os, Ir, Rh

- Solvent that can be purified
  - Lower purity suitable for secondary use

<u>Do NOT Recycle (examples)</u>

- Gas cylinders past their pressure testing date
- Used disposable pipettes and syringes
- Chemicals and assay kits past their expiration
- Obviously degraded chemicals
- Used tubing, gloves and wipes

Do NOT recycle if it presents a safety or security hazard

Waste: Recycling

Solvents

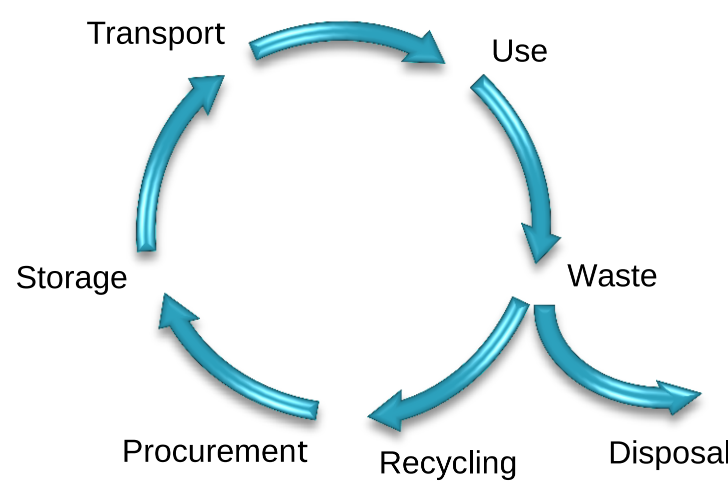
- Distillation or Evaporation
- Keep solvents segregated prior to separation
- Avoid contamination due to careless handling
  - Requires good labeling
    - A small amount of the wrong chemical can ruin a desired separation
- Azeotropes may prevent separation
- Boiling points must be widely different

- Be aware of hazards
  - Do not evaporate or distill corrosive, radioactive, peroxides or peroxide formers
  - Beware toxics and flammables
  - Use proper ventilation

Waste: Disposal

- If using a disposal service:
  - Are there regulations?
  - Permits/licensing requirements?
  - How will waste be packaged?
  - How will waste be transported?
  - Where and how will waste be disposed?
  - Where does your liability end?
    - Incineration vs. landfill
    - Maintain records

- **When is the best time to figure out how to dispose of waste?**



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Waste: Disposal

- Emissions from incineration vs. open burning

	Open Burn (µg/kg)	Municipal Waste Incinerator (µg/kg)
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2

Source: EPA/600/SR-97/134 March 1998

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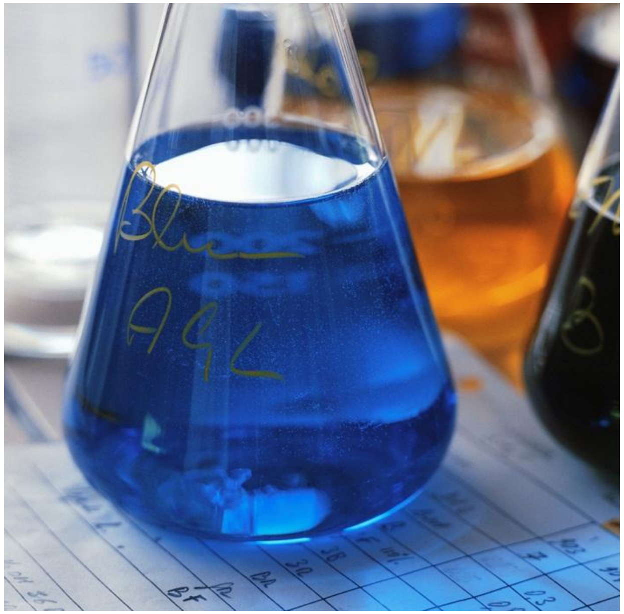
Waste: Orphans and Unknowns

Preventing Orphan Chemicals and Waste

- Have a checkout procedure for those leaving the laboratory
- For chemicals and samples being kept
  - Label all carefully
  - Document in lab notebook and elsewhere
- Dispose of all unneeded or excess chemicals
  - Put into chemical exchange program
  - Dispose of as hazardous waste



Everything left behind has a new owner

Waste: Orphans and Unknowns

Dealing with Unknown Chemicals and Waste, "Legacy" Waste

- Avoid creating
- Not necessary to know exact identity
  - Need hazard information for disposal
- Consider more serious hazards first
  - Radioactive, explosive, bio-waste
- Look for hints from container, physical characteristics, location found, talk to other people
- Before handling, prepare for the worst
- Test
  - pH
  - Reactivity
    - Air, water, flammability, redox
  - Solubility
  - Qualitative analysis for presence of heavy metals, cyanide, etc.

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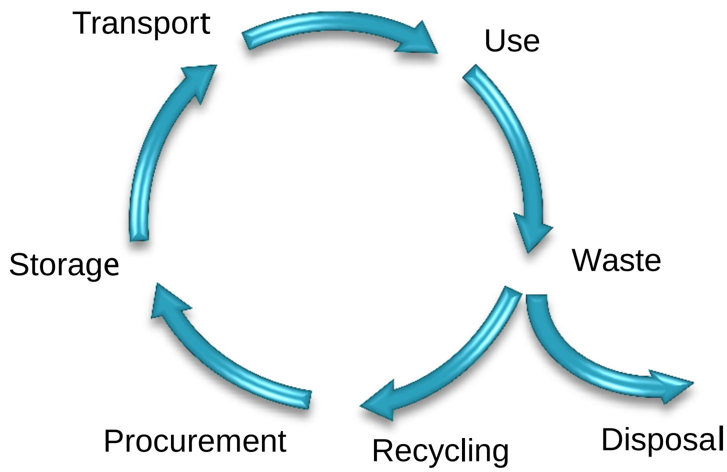
Activity: Chemical Management Assessment

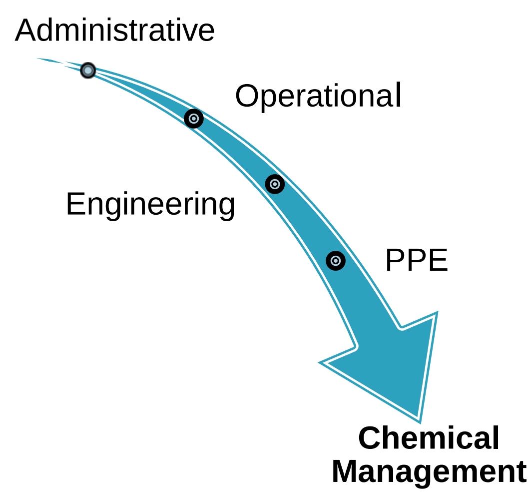
- Get in the groups of 3-5 people from the Lab Assessment activity

- Assess how your lab handles chemical management at all stages of the chemical life cycle

- Create a plan for improving chemical management in your lab
  - Consider all levels of CSS controls
  - What support or resources are needed?
  - Who will need to be a part of the effort?

Take about 40 minutes to do this





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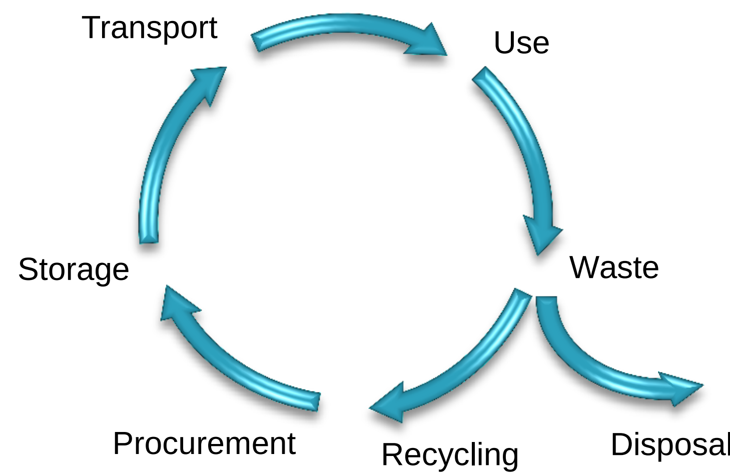
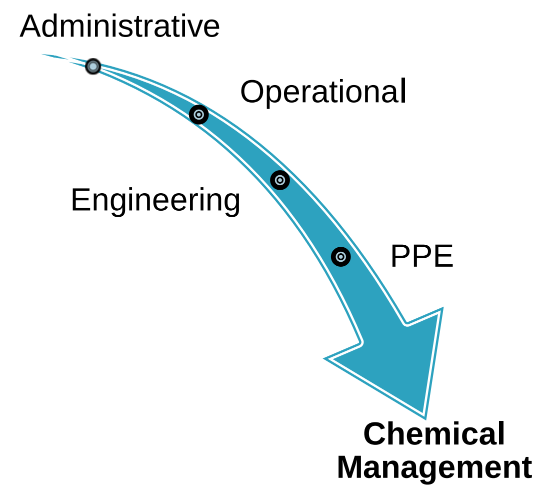


Chemical Management: Conclusions

- Key to chemical safety and security
- Involves all CSS controls
- Many issues addressed by planning ahead
- Best practices in chemical management and high quality research are positively correlated
- Opportunities for those willing to pioneer improvements



Evaluations

- Please find the evaluations page for this module in your workbook

Thank you for your participation!

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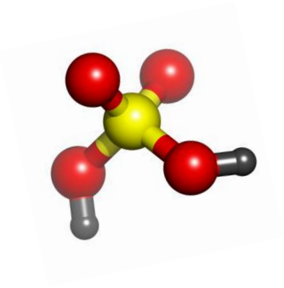
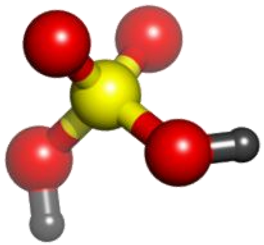


Tea Break!



Industrial Ventilation

SAND No. 2012-1603C
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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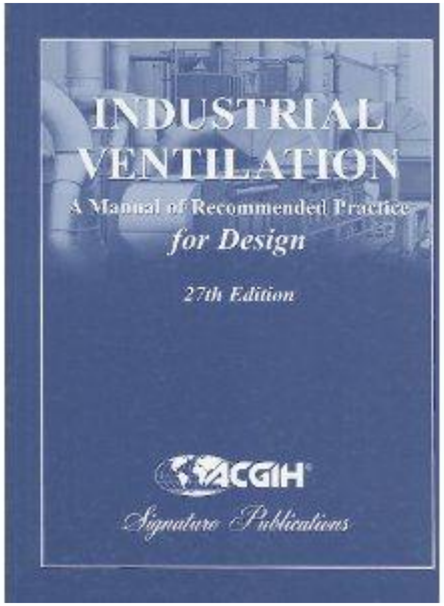
Sandia
National
Laboratories

Topics

- Definitions
- Common Terminology
- Purpose
- Hazard Assessment
- General Ventilation
- Local Exhaust Ventilation
- Ventilation Evaluation
- Troubleshooting
- Exercises



American Conference of Governmental Industrial Hygienists (ACGIH) Ventilation Manual 27th Edition
http://www.acgih.org/store/ProductDetail.cfm?id=1905

Definitions

- Heading, ventilating and air conditioning (HVAC):refers to the distribution system for heating, ventilating, cooling, dehumidifying and cleansing air.
- Replacement/Supply air: refers to replacement air for HVAC and local exhaust ventilation.
- General ventilation: refers to ventilation that controls the air environment by removing and replacing contaminated air before chemical concentrations reach unacceptable levels.
  - Local exhaust ventilation (LEV): refers to systems designed to enclose, or capture and remove contaminated air at the source.

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Common Terminology

Q = volume of air in cubic meters

V = velocity of air in meters per second

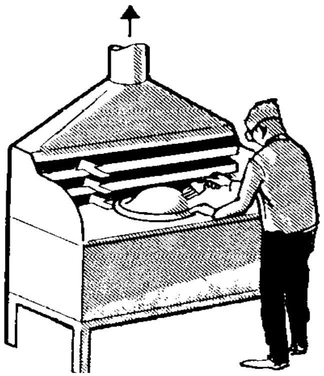
- Duct velocity-velocity required to transport the contaminant
- Face velocity-velocity on the front of an enclosing hood
- Capture velocity-velocity required to capture contaminant at point of generation

A = cross sectional area of hood opening in square meters

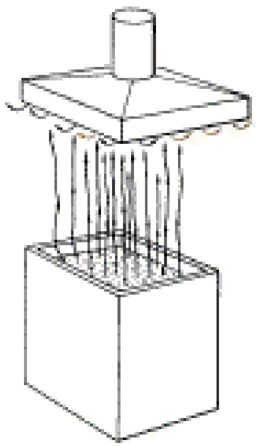
X = distance of ventilation from the source in meters

Purposes of Industrial Ventilation

- Protect workers from health hazards
  - *Dilute, capture, or contain* contaminants
- Protect workers from hot processes
  - *Ovens, foundries*
- Protect the product
  - *Semiconductor*
  - *Electronics*
  - *Pharmaceuticals*



Slot Hood



Canopy Hood

Purposes of Industrial Ventilation

- Emergency ventilation
  - Standalone fans
  - Detectors connected to ventilation or scrubber systems
  - Safe room
    - Positive pressure
- Enclosed vented rooms or cabinets
  - Gas cabinets
- Comply with health and safety regulations

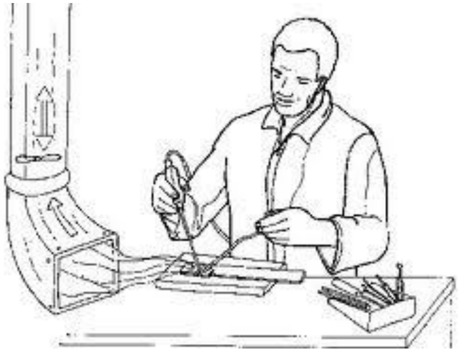
Photo credit: Advanced Specialty Gas Equipment

Photo credit: Emergency Responder Products

Hazard Assessment

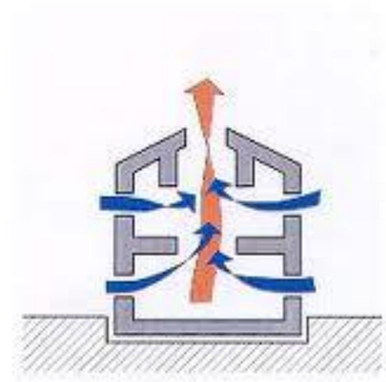
- What are the airborne contaminants?
  - Particles
  - Solvent vapors
  - Acid mists
  - Metal fumes
- How do to the workers interact wit source contaminant?
- Are workers exposed to air contaminants in concentrations over an exposure limit?

  *Requires air monitoring of the task
- Dilution or local exhaust ventilation?



Picture Credit : International Labor Organization

General Ventilation



- Natural Ventilation:
  - Useful for hot processes
  - Chimney effect
  - Windows and doors kept open
- Example: a warehouse opens the windows to create natural ventilation

  $Q = 0.2\ AV$

  A = square meters (area of open doors)

  V = wind speed in kilometers/hour

  Q = estimates the volumetric flow rate through the building (m^3/s)

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General Ventilation

Dilution Ventilation

-Heat control

-Dilution of odors, flammables

-<u>Not</u> for control of toxics

Principles

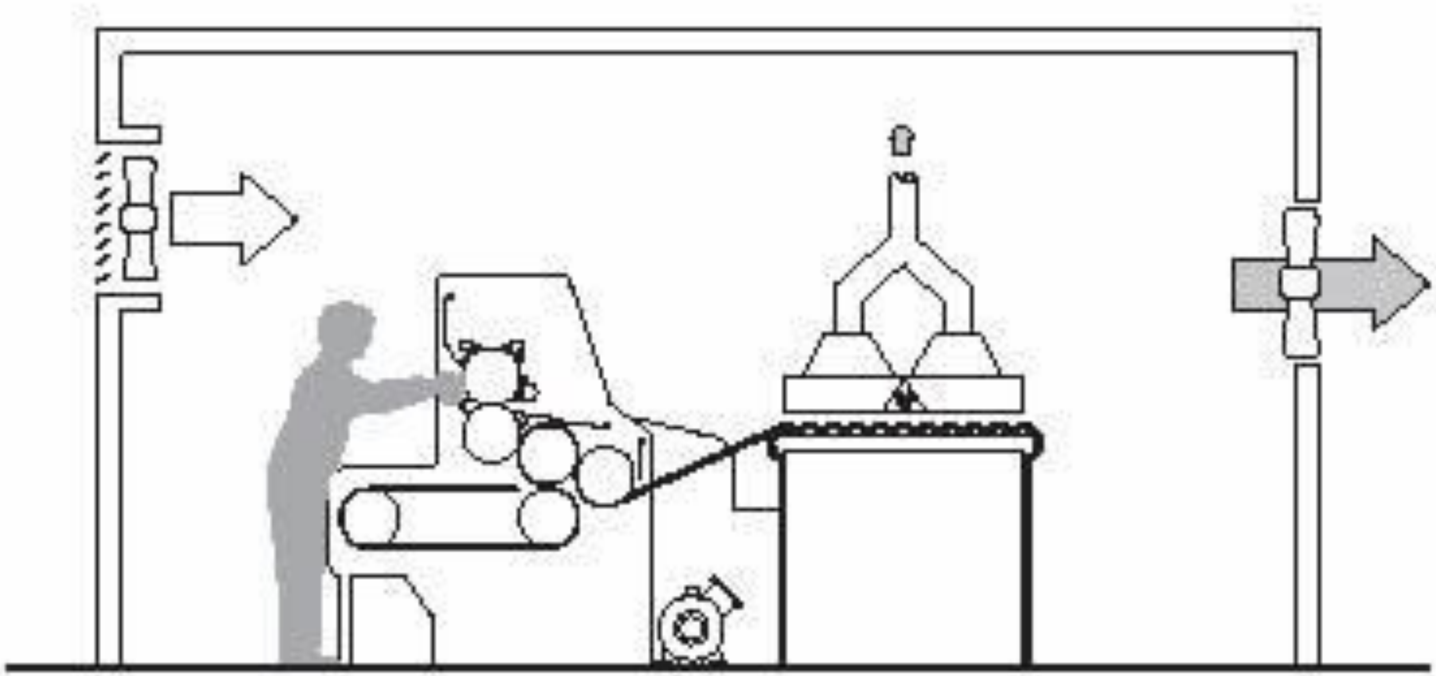
-Contaminant emissions must be widely dispersed

-Exhaust openings must be near contaminant source

-The worker must not be downstream of contaminant

-Air flow over worker should not exceed 3.5 meters/sec

General Ventilation



General ventilation for cleaning a printing press

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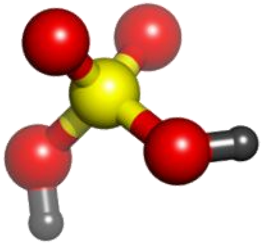

Local Exhaust Ventilation (LEV)

- Use when contaminant concentration cannot be controlled by dilution ventilation or other controls
- Select the type of LEV from hazard assessment
  - Which type is best to capture the contaminant?
    - Enclosed or capture hood?
    - Consider worker's needs
  - What duct transport velocity is required to carry the contaminant? Heavy particles?
  - What face or capture velocity is required?
- Select duct material for the contaminant
- Ensure enough replacement air/adequate fan size

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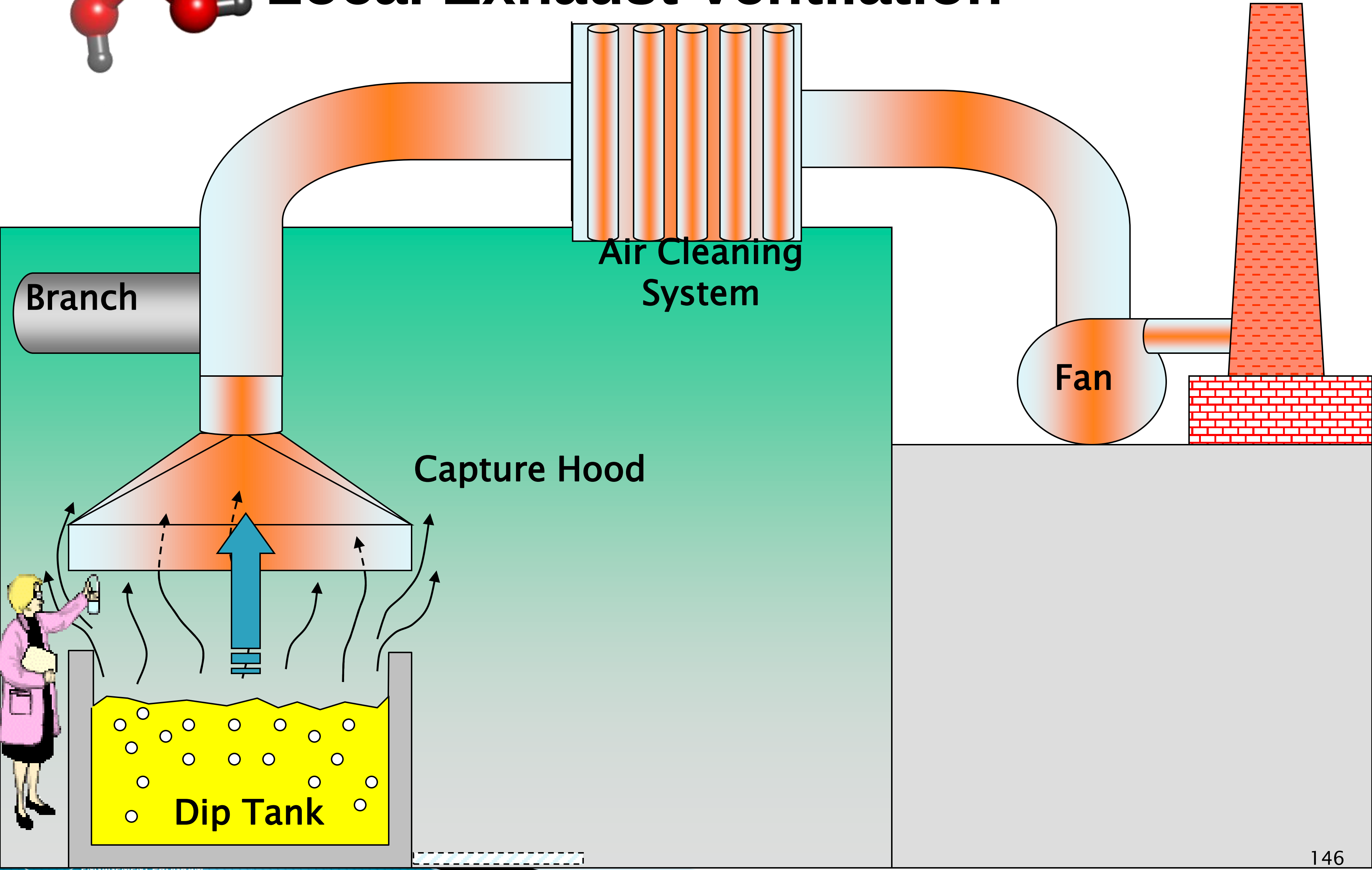
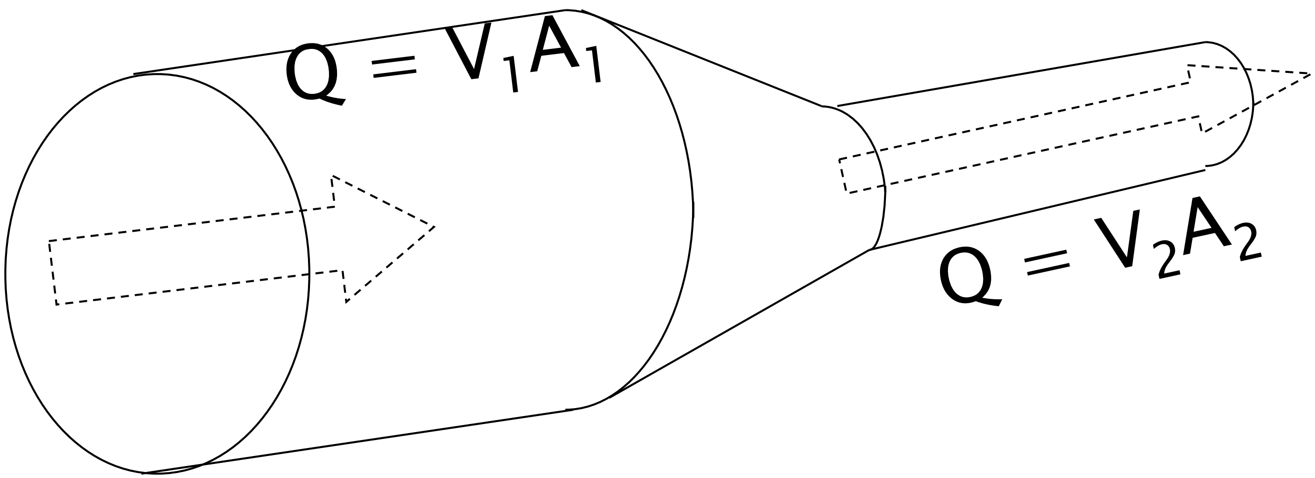
Local Exhaust Ventilation



Local Exhaust Ventilation

Volumetric Flow Rate, Q = VA [**Circular Opening**]

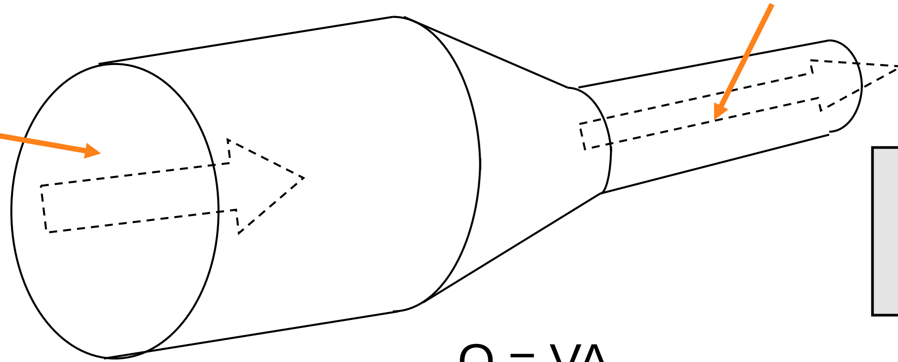


Q = Volumetric flow rate, in cubic meters/second
V = Average velocity, in meters/second
A = Cross-sectional area in square meters

Local Exhaust Ventilation

Duct diameter = 1 meter
V = 600 meters/second
What is Q?

Duct diameter = 0.5 meter
What is the duct velocity (V)?



For circular ducts
$A = \pi d^2 / 4$

Q = VA

Q = (600 m/s)(π[1m]^2/4)

Q = **471 meters^3/second**

Q = VA

471 meters^3/s = V (π[0.5m]^2/4)

V = 2400 meters/second

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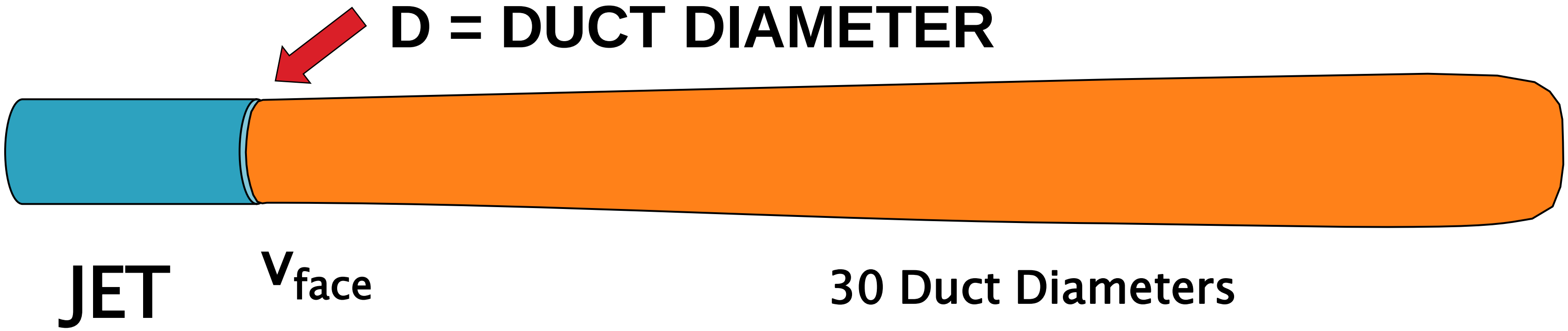
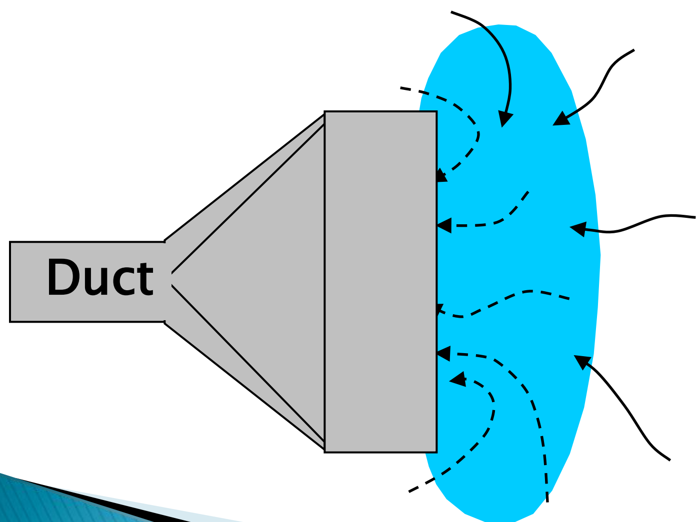
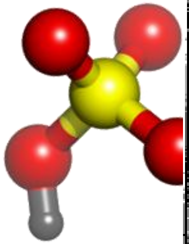
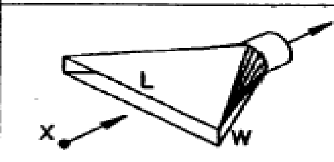
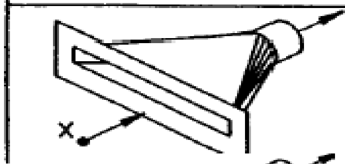
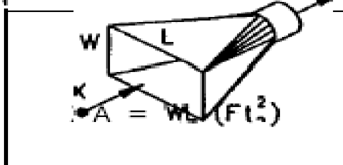
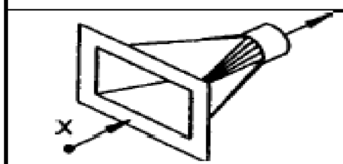
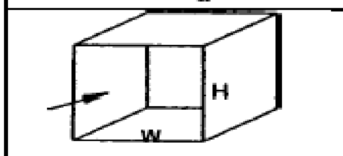
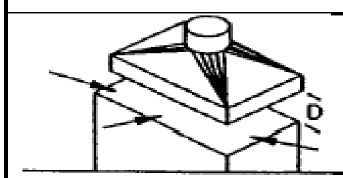
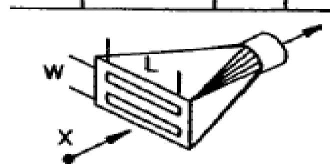
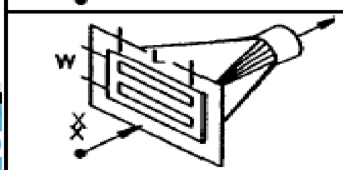
Local Exhaust Ventilation





Capture of contaminant is only effective within <u>one (1) duct diameter</u>



HOOD TYPE	DESCRIPTION	ASPECT RATIO, W/L	AIR FLOW
	SLOT	0.2 OR LESS	$Q = 3.7\ LVX$
	FLANGED SLOT	0.2 OR LESS	$Q = 2.6\ LVX$
	PLAIN OPENING	0.2 OR GREATER AND ROUND	$O = V(10X^2 + A)$
	FLANGED OPENING	0.2 OR GREATER AND ROUND	$Q = 0.75V(10X^2 + A)$
	BOOTH	TO SUIT WORK	$Q = VA = VWH$
	CANOPY	TO SUIT WORK	$Q = 1.4\ PVD$ SEE FIG. VS-99-03 P = PERIMETER D = HEIGHT ABOVE WORK
	PLAIN MULTIPLE SLOT OPENING 2 OR MORE SLOTS	0.2 OR GREATER	$Q = V(10X^2 + A)$
	FLANGED MULTIPLE SLOT OPENING 2 OR MORE SLOTS	0.2 OR GREATER	$Q = 0.75V(10X^2 + A)$

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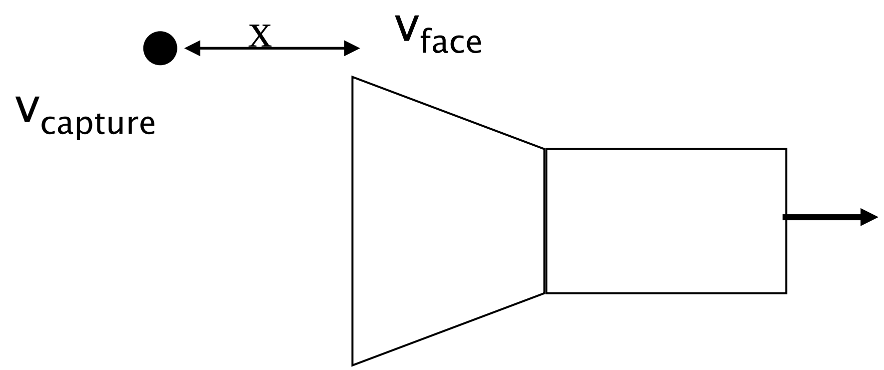
ACGIH Ventilation Manual

Local Exhaust Ventilation

Capture Velocity (V) : [Plain Opening]



$Q = V\ (10x^2 + A)$

X = distance of source from hood face

Recommended Capture Velocities

CONDITION	EXAMPLES	CAPTURE VELOCITY Range in meters/second
No velocity, Quiet air	Evaporation from tanks, degreasers	0.25 – 0.5
Low velocity, moderately still air	Spray booths, container filling, welding, plating	0.5 – 1.0
Active generation into rapid air motion	Spray painting (shallow booths), crushers	1.0 – 2.5
High initial velocity into very rapid air motion	Grinding, abrasive blasting, tumbling	2.5 – 10.1

ACGIH Ventilation Manual

Recommended Duct Velocities

CONTAMINANT	EXAMPLES	DUCT VELOCITY Meters/second
Vapors, gases, smoke	Vapors, gases, smoke	5.0 – 10.1
Fumes	Welding	10.1 – 12.7
Very fine dust	Cotton lint	12.7 – 15.2
Dry dusts & powders	Cotton dust	15.2 – 20.3
Industrial dust	Grinding dust, limestone dust	17.8 – 20.3
Heavy dust	Sawdust, metal turnings	20.3 – 22.9
Heavy/moist dusts	Lead dusts, cement dust	> 22.9

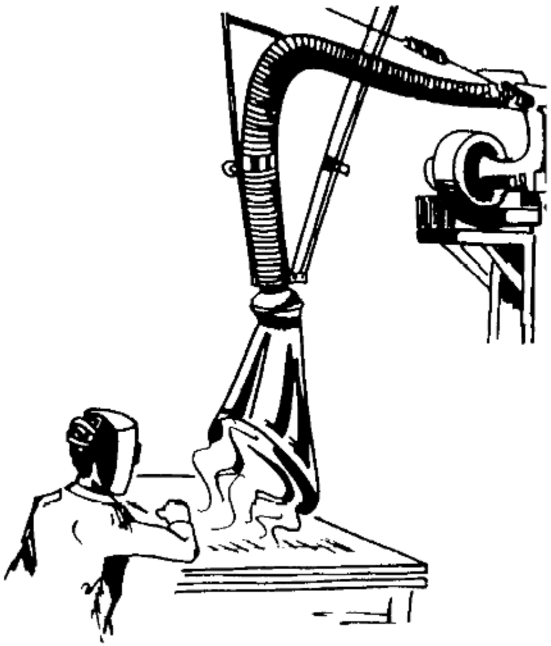
ACGIH Ventilation Manual

Local Exhaust Ventilation

- Canopy hood:
  - Best for controlling hot processes
  - Not good for capturing dusts, or vapors
  - Not good where cross-drafts exist
  - Worker must not put head under canopy

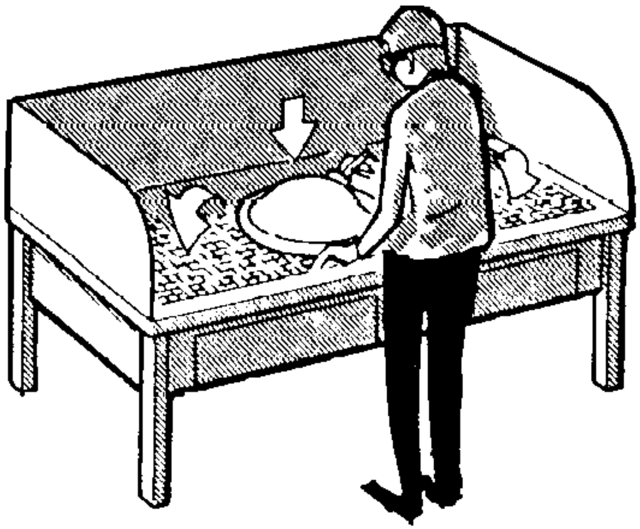
Local Exhaust Ventilation

- "Elephant trunk":
  - Good for welding fumes, small process tasks, machining, disconnecting process lines
  - Place close to contaminant
  - Ensure adequate capture velocity at distance from contaminant
  - *Flanged* opening captures contaminant better



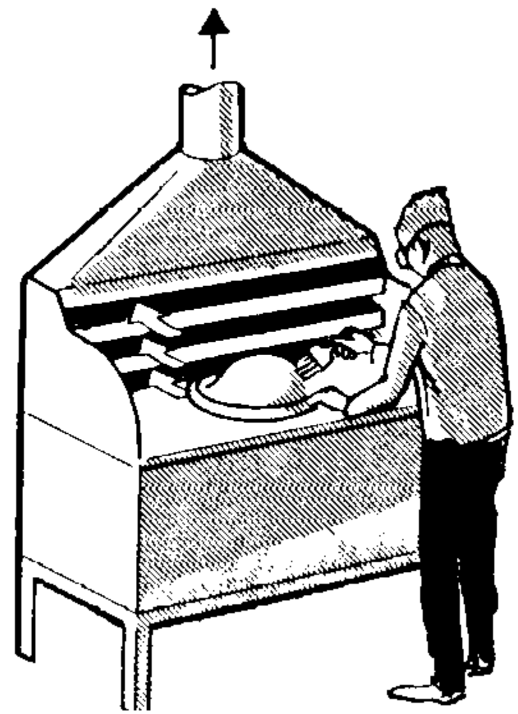
Local Exhaust Ventilation

- Downdraft hood:
  - Vapors pulled down through grill
  - Capture velocity depends on source distance from grill
  - <u>Not</u> for hot operations



Local Exhaust Ventilation

- Slot ventilation:
  - Best for liquid open surface tanks
    - Acid baths
    - Plating tanks
  - Pulls air across the tank away from worker
  - Side enclosures prevent cross drafts
  - Push-Pull design is optional (push jet)



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Local Exhaust Ventilation

- Fume hood:
  - Laboratory use
  - Best for small amounts of chemicals
  - Sash must be kept at set level
  - NO storage of equipment in the hood!

Local Exhaust Ventilation

- Enclosures:
  - Example:
    - Paint booths
  - Control of exposure to liquid aerosols and vapors
  - Flammability hazard
  - Must have scheduled filter changeout
  - Operator must be upstream

Local Exhaust Ventilation

- Other vented enclosures
  - Glove boxes
  - Furnaces/ovens
  - Abrasive blasting

Photo credit: Borel Furnaces and Ovens

Photo credit: U. S. Department of Labor. OSHA

Local Exhaust Ventilation

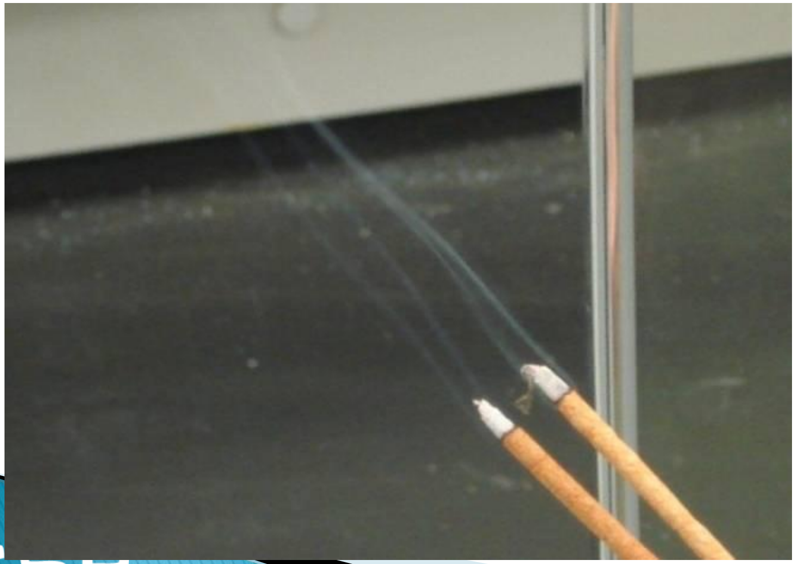
Exhaust Systems:

- Do not place exhaust stack near air intakes
  - Re-entrains contaminants into the building
- Do not use rain caps
- Stack height depends on:
  - Contaminant temperature
  - Building height
  - Atmospheric conditions
  - Discharge velocity
  - Ideal discharge velocity is 15 meters per second

Ventilation System Evaluation

- Evaluate capture velocity
  - Quantitatively-anemometers, velometers
  - Qualitatively-smoke tubes,
    - Visualizes air movement
    - Use water vapor for clean rooms

Photo Credit: All Products Inc.



Ventilation System Evaluation

- Air velocity measurements
  - Measure air velocities (meter/sec) at a number of points
  - Average the results and determine volumetric flow rate: Q = VA
  - All instruments must be calibrated periodically
  - Types:
    - Swinging vane velometer
    - Hot-wire anemometer

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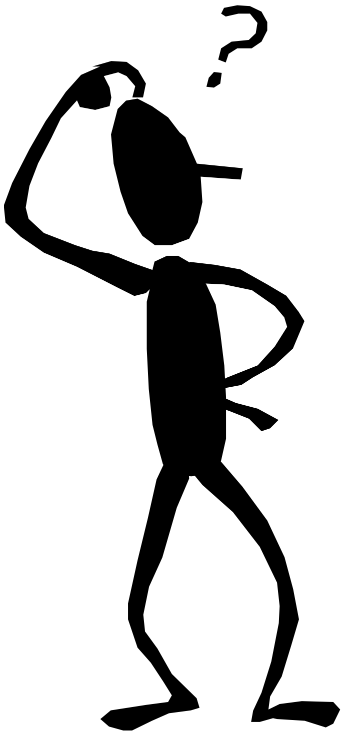
Troubleshooting

- Wrong hood for process
  - Example: canopy hood for toxics
- Insufficient capture velocity
- Insufficient duct velocity
  - ~14 meters/second for vapors
  - ~18 meters/second for dust
- Too much air flow = turbulence
- Traffic or competing air currents
- Insufficient make up air
  - Negative pressure
  - Can’t open doors



Exercise

- What is the preferred ventilation system for the following situation?
  - Dilute non-toxic odors in the warehouse

A) General ventilation

B) Local exhaust ventilation

Exercise

- What is the preferred ventilation system for the following situation?
  - Acid processing bath with open surface area

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Welding table

A) Lab fume hood

B) Slot ventilation

C) Elephant trunk

D) Canopy hood

E) Paint booth

Exercise

- What is the preferred ventilation system for the following situation?
  - Chemical analysis of small samples for quality control

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

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Exercise

- What is the preferred ventilation system for the following situation?
  - Spray painting a large piece of equipment

A) Lab fume hood
B) Slot ventilation
C) Elephant trunk
D) Canopy hood
E) Paint booth

US Standards & Guidelines

ACGIH

American Conference of Governmental Industrial Hygienists

Industrial Ventilation, A Manual of Recommended Practice

AIHA

American Industrial Hygiene Association

Standard Z9.2, Fundamentals Governing the Design and Operation of Local Exhaust Ventilation Systems

ASHRAE

American Society of Heating, Refrigeration and Air Conditioning Engineers

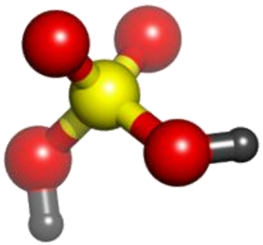
Standard 62.1-2010, *Ventilation for Acceptable Indoor Air Quality*

OSHA

Occupational Safety and Health Administration

Ventilation, 29 Code of Federal Regulations 1910.94

http://osha.gov/



Fire Prevention and Protection in the Laboratory

Fires

- Preventable
- Caused by unsafe practices
  - Electrical safety violations
  - Uncontrolled use of flammable and combustible materials
- Control
  - Inspect, inspect, inspect

  Educate, educate, educate!

Home Fires

1 million fires and 8,000 deaths annually in the US

Leading causes:
- Cigarettes
- Heating/cooling equipment
- Electrical
- Matches, lighters, candles

Industrial Fires

- **Fifth leading cause of accidental death**
  - Vehicles, falls, poison, drowning, fire
- **Most dangerous industries from fire hazard:**
  - Mines
  - Grain elevators and mills
  - Refineries
  - Chemical plants
- **Leading causes:**
  - Electrical
  - Smoking
  - Friction
  - Overheating
  - Hot surfaces

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Key Elements of Fire Safety

Get occupants out

Minimize property loss and interruption

Fire Containment/Suppression

Common Myths

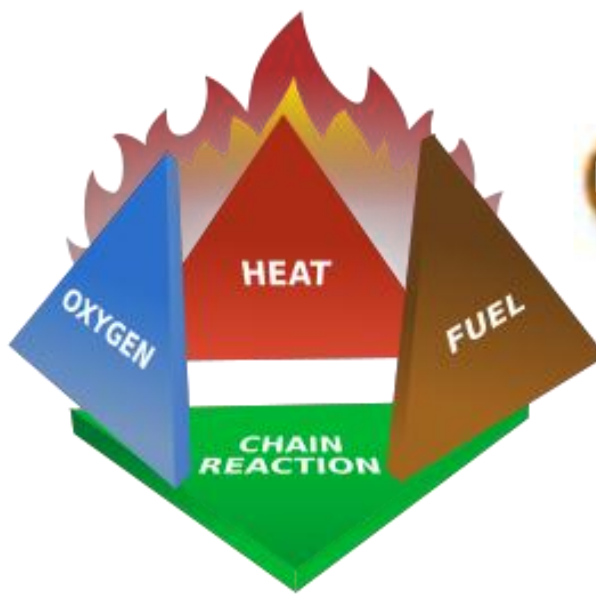
- **Fire will light the way out**
  - Smoke cloud & soot
- **Plenty of time to escape**
  - 1 min from small to inescapable fire
- **People are killed by the flames**
  - #1 killer in fires is CO, not flames
- **Wait to be rescued**
  - No! Act to save self
  - Ladders can reach to about 6th floor
- **Can not prepare for a fire**
  - Preparation can save your life

It’s the Smoke…

Facial Burns

Fire

- A fire must have four things to ignite and maintain combustion:
  - Fuel
  - Heat
  - Oxygen
  - Chain reaction



Flash Point

- Flash point:
  - The minimum temperature at which a liquid gives off enough vapor to form an ignitable mixture.
  - In general, the lower the flash point, the greater the hazard.
- Flammable liquids:
  - have flash points below 38ºC
  - are more dangerous than combustible liquids
  - may be ignited at room temperature
- Combustible liquids:
  - have flash points at or above 38ºC
  - Can pose serious fire and/or explosion hazards when heated

Flammability/Explosive Limits

Above UFL/UEL, mixture is **too rich to burn**

Upper Flammability/Explosive Limit (**UFL/UEL**)

Flammability/Explosive Range

Lower Flammability/ Explosive Limit (**LFL/LEL**)

Below LFL/LEL, mixture is **too lean to burn**

Defined in terms of the amount of fuel in air.

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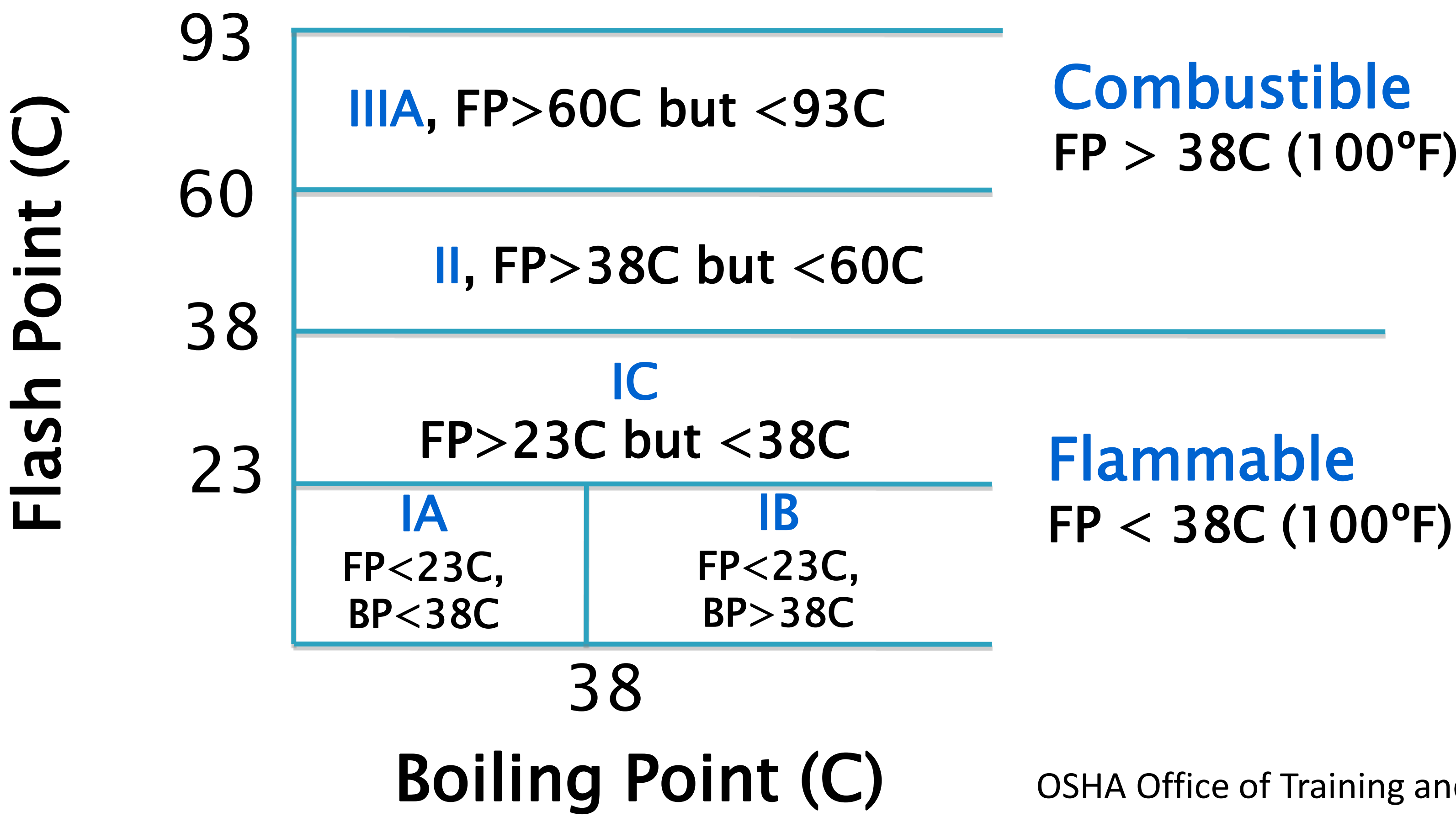
Classes of Flammable and Combustible Liquids



OSHA Office of Training and Education, defined in Fahrenheit

182

Classes of Some Flammable Liquids

	Common Name	Flash Point (C)
CLASS IA	Ethyl Ether	– 45
CLASS IB	Gasoline	– 43
	Methyl Ethyl Ketone	– 6
	Toluene	4
CLASS IC	Xylene	27 – 46
	Turpentine	35

OSHA Office of Training and Education

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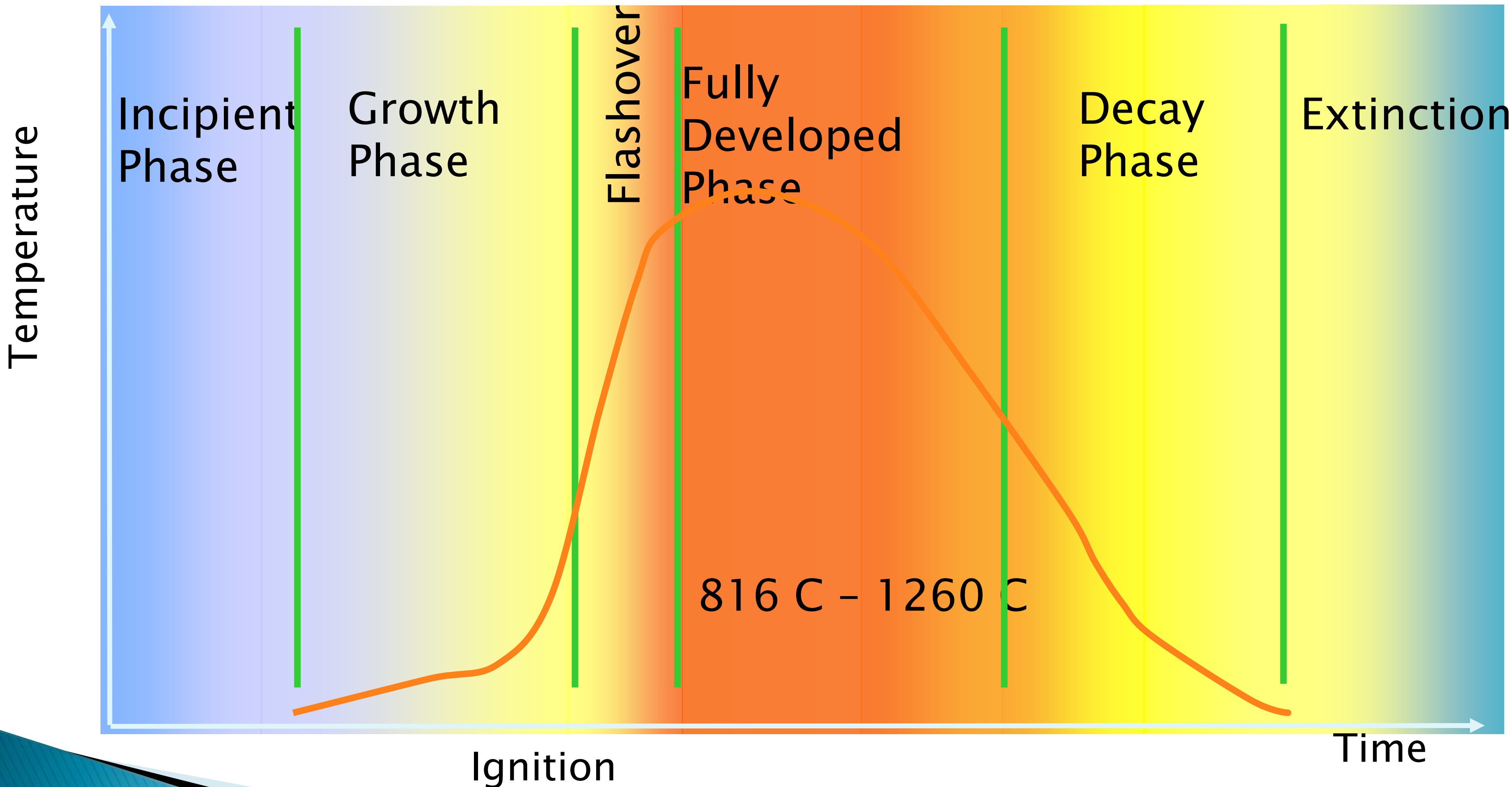
Fire Safety Program Components

A good plan for safe use of flammable and combustible liquids contains at least these components:

- Control of ignition sources
- Proper storage
- Fire control
- Safe handling

Fire Behavior



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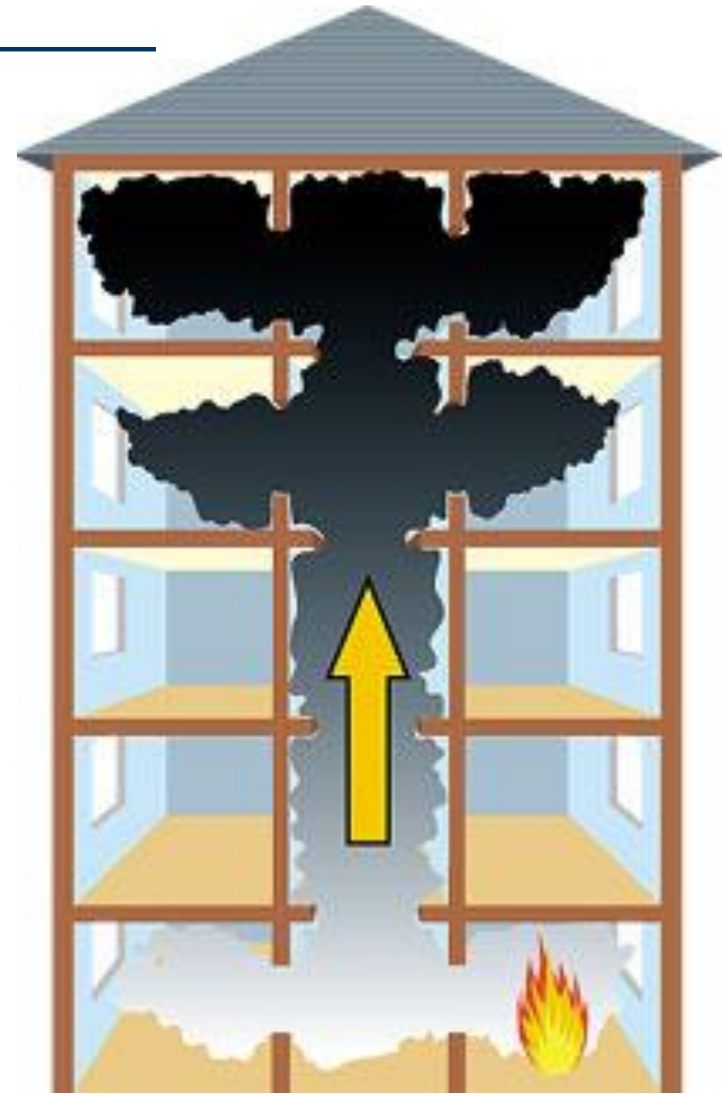
Fire Behavior

Stack Effect

- Hot expanding gases move vertically
  - Tightness of construction
  - External winds
  - Internal/external temperature
  - Vertical openings
    - Stairways
    - Elevator shafts
    - Ventilation shafts



Vapor Volume

Volume of gas formed when a liquid substance evaporates

Computed from specific gravity and vapor density

$$\text{Vapor Volume } (m^3/\text{liter}) = \frac{0.829\ (\text{SpG})}{\text{Vapor density}}$$

Example: What is the vapor volume of a liter of acetone?
[SpG = 0.9, relative to water; Vapor density = 2, relative to air]

$$\text{Vapor Volume } (m^3/l) = \frac{0.829\ (0.9)}{2} = 0.373\ m^3/l$$

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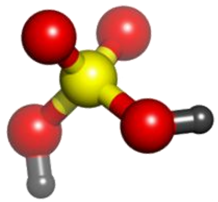

Vapor Volume

What is the probability of forming a combustible mixture if a 4 liter container of acetone is used in a room 3 x 4 x 2.5 m?

[LEL = 2.5%; assume incomplete mixing factor 5]

Volume of the space = 30 m^3

Vapor volume = 0.373 m^3/L

Vapor volume necessary to form a Combustible mixture:

$$30\ m^3 \times 0.025 = 0.75\ m^3$$

$$\frac{0.75\ m^3}{0.373\ m^3/\ L} = 2.01\ L$$

Applying the mixing factor of 5:

2.01 L / 5 = 0.40 L

[About = 1 coffee mug]

Since it doesn't take much more than "1 coffee mug" of acetone to form a combustible mixture, the probability appears to be high!

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Housekeeping…

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Flammable Liquid Containers

Tool Cleaning (Acetone)

Fire Hazards

- **Sources of fuel**
  - Flammable liquids
  - Flammable gases
  - Wood, paper, cardboard
  - Oil soaked rags

Train employees to notice & report fire hazards

Periodic inspections

Drills

- **Sources of heat (ignition)**
  - Electrical circuits:
    - Shorts, sparks
    - Arcs (switches)
    - Heat build-up
  - Hot surfaces
  - Space heaters
  - Hotplates, coffee pots, coffee makers
  - Welding
  - Smoking
  - Open flames
  - Static electricity

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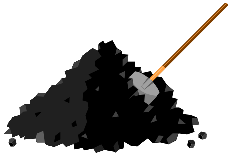
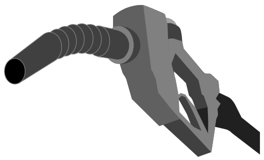
Classification of Fires

With recommended extinguisher distances

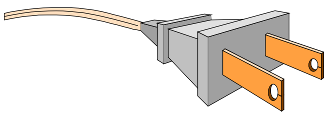
- **A Ordinary combustibles – cloth, paper, wood, coal** **~23 m**
  - Extinguish by cooling or smothering



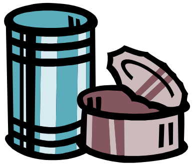
- **B Flammable/combustible liquids, gases, greases and oils - gasoline, diesel fuel** **~15 m**
  - CO_2 or dry powder: monoammonium phosphate



- **C Energized Electrical equipment cables, motors** **nearby**
  - Extinguishing agent must ***not*** be conductive
  - CO_2 or dry powder



- **D Combustible metals - sodium, magnesium, titanium** **~23 m**
  - Extinguishing agents must absorb heat and not react with the metal
  - special dry powder, sand



- **K Restaurant grease fires associated with cooking** **nearby**
  - Special liquid chemicals

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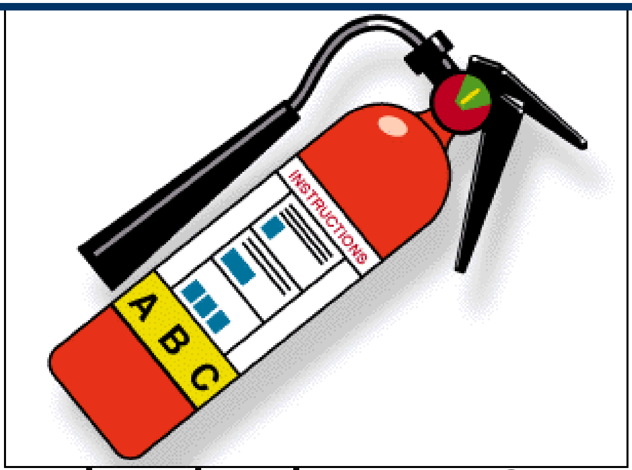
Fire Extinguishers

Dry Chemical

Water



Placed within ~15-25 m

Annual & Monthly inspections

CO_2

Fire Alarm Systems

- **Will it be recognized and followed?**
  - Audible, visual, public address systems…
- **What about deaf or blind employees?**
  - Are there “dead spaces”…
- **System reliability**
  - System failure may not be obvious
  - Supervised systems (built-in monitoring)
  - Testing, maintenance and backup systems

Fire Detection & Alarms

- **Thermal**

- **Heat**
  - Fixed temp
  - Rate of rise
    - ~6 to 8 C/min (12 to 15ºF/min)

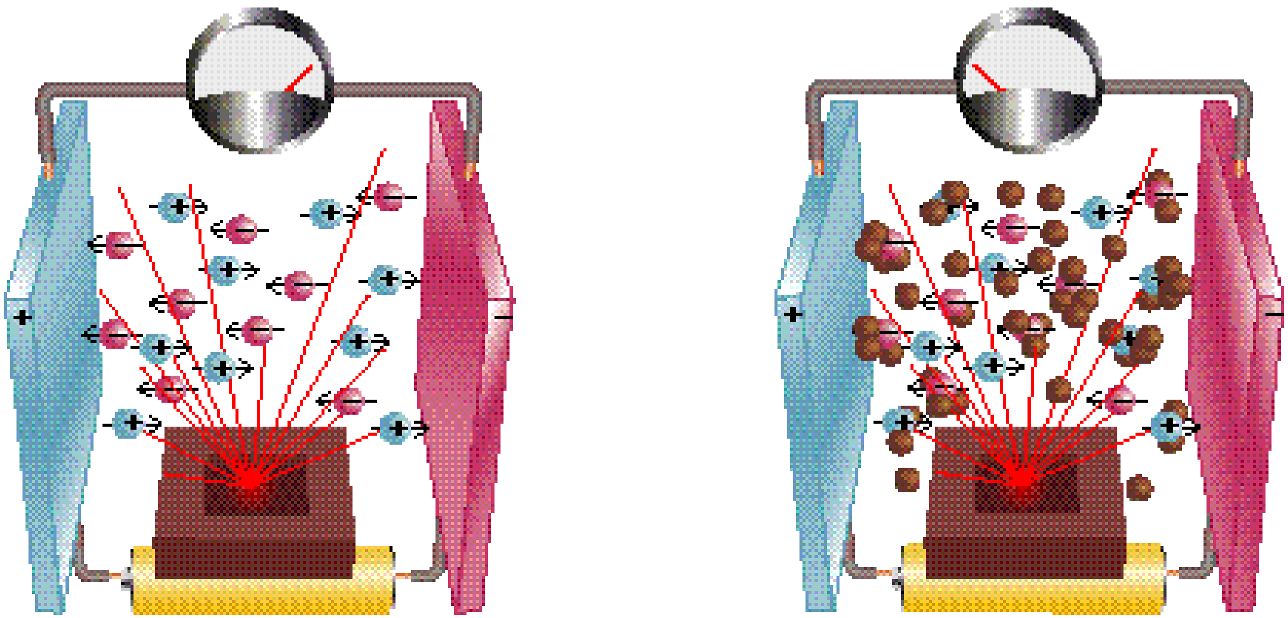
Issues:

Testing

Dust, corrosion, hot processes, weather, mechanical damage

- **Smoke**
  - Photoelectric
    - IR from smoke
  - Ionization
    - Ionize smoke
- **Flame Detectors**
  - Flames – IR or UV
- **Gas Sensors**

Smoke Detectors



- Alpha particles from Americium-241 (red lines) ionize the air molecules (pink and blue spheres).
- The ions carry a small current between two electrodes.
- Smoke particles (brown spheres) attach to ions reducing current and initiate alarm.

False Alarms

False alarms may be triggered by construction dust created during renovations

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Manual Pull Stations

- Manual Pull Stations are devices located on the wall (usually near an exit)
  - Sends a signal to the building's fire alarm system when activated
  - Places the building into alarm

People are reluctant to sound fire alarms!

Responding To A Fire

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Employee Training

Few employees know how to *effectively* use extinguishers!

Need for training:

- Initial training
- Annual refresher

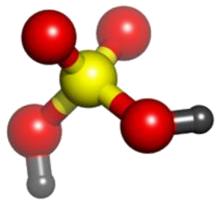
Using a Fire Extinguisher

Video Courtesy of Washington State Emergency Management Division, Public Education Program

P	Pull
A	Aim
S	Squeeze
S	Sweep

Electrical Fires

- Pull the plug out or switch off the power at the fuse box. This may stop the fire immediately.
- Smother the fire with a fire blanket, or use a dry powder.
- Never use water on it.



What To Do If Someone Catches On Fire

If *you* should catch on fire:

STOP – where you are
DROP – to the floor
ROLL – around on the floor

This smothers the flames, possibly saving your life.

Remember STOP, DROP and ROLL

If a *co-worker* catches on fire:

Smother flames by grabbing a blanket or rug
Wrap them in it.
Could save them from serious burns or death.

When Not To Fight A Fire

Don’t fight a fire, when:

- It is bigger than a waste paper bin
- One extinguisher is not enough
- The fire is spreading beyond the spot where it started
- Smoke is affecting your breathing
- You can't fight the fire with your back to an escape exit
- The fire can block your only escape
- You don't have adequate fire-fighting equipment

DON'T FIGHT THE FIRE YOURSELF

CALL FOR HELP

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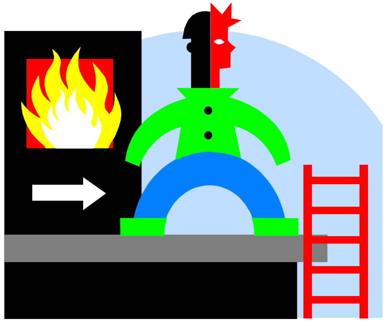
Remember

When…



- The extinguisher runs out of agent
- Your path of escape is threatened
- The extinguisher proves to be ineffective
- You are no longer be able to safely fight the fire

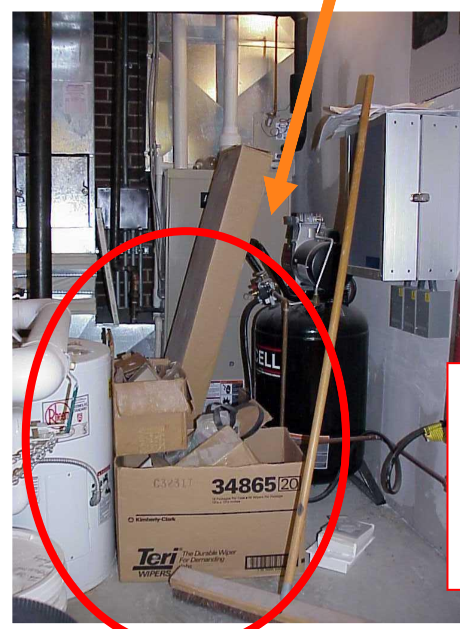
…LEAVE THE AREA IMMEDIATELY!

Storage Guidelines

- All storage must be at least 1 m from electrical panels. In some emergency situations it will be necessary to access these panels quickly.

Improper Storage in front of Electrical Panel

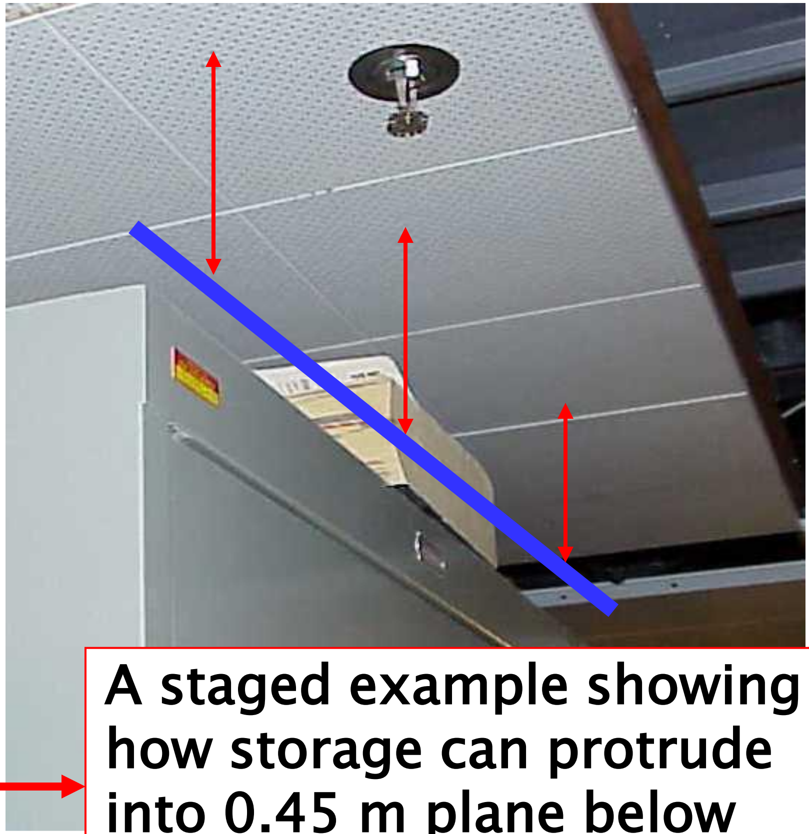
- Maintain at least 1 m clearance from heating surfaces, air ducts, heaters, and lighting fixtures.
- Storage of combustible materials in mechanical rooms is prohibited.



Improper Mechanical Room Storage

Storage Guidelines

- No storage is allowed in corridors and stairwells. A cluttered hallway could slow down emergency evacuation.
- Storage must not exceed a plane of 0.45 m below sprinkler heads or smoke detectors. Storage that breaks this plane may prevent sprinkler heads from fully covering room during a fire.



A staged example showing how storage can protrude into 0.45 m plane below sprinkler heads.

Myths about Sprinkler Systems

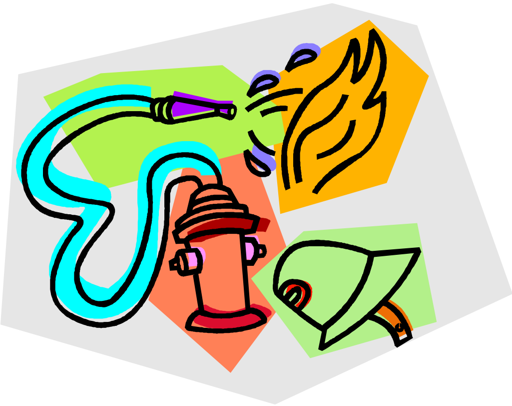
- **A sprinkler system will cause excessive water damage**
  - Sprinklers use a fraction of water compared with a fire hose.
  - Sprinklers release ~30 – 100 liters per minute compared to a fire hose at ~200 – 500 liters per minute.
  - Sprinklers operate very early in the fire development, and consequently require a smaller quantity of water.
- **When a fire occurs, every sprinkler head goes off**
  - Sprinkler heads are individually activated by fire.
  - $>$ 50% of the fires are controlled by $\leq$ 4 sprinkler heads, and in many instances fires are controlled with one sprinkler.
- **The pipes burst due to freezing**
  - Sprinklers can be protected with various forms of frost protection, such as installing a dry system or providing heating elements to protect the sprinkler systems.

Myths about Sprinkler Systems

- **Sprinkler systems might accidentally go off**
  - Sprinklers are very reliable; the chances of going off without mechanical assistance are 1 in 16 million; Fork lift truck drivers soon learn to avoid them.
- **Smoke detectors provide enough protection**
  - Smoke detectors provide early warning and save lives, but do nothing to extinguish a fire or protect those physically unable to escape on their own.
  - Too often, battery operated smoke detectors fail to function because the batteries are dead or have been removed.
- **Sprinklers are designed to protect property, but are not effective for life safety**
  - Sprinklers can reduce property losses up to 85%.
  - Combining sprinklers and early warning systems can reduce overall injuries, loss of life and property damage by 50%.

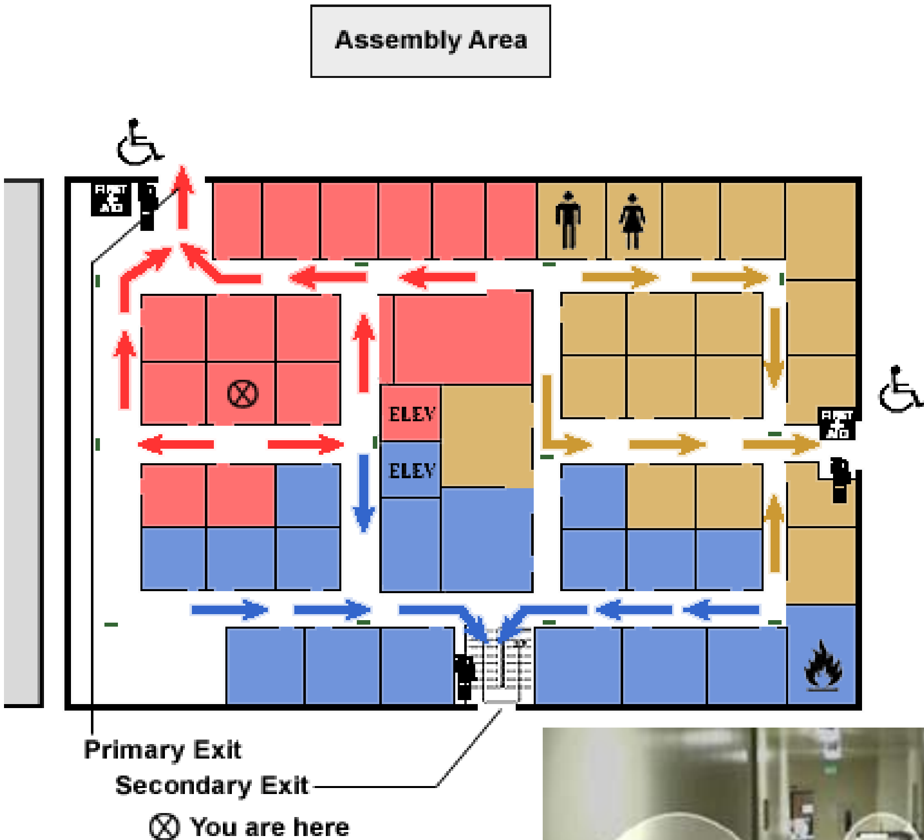
Fire Safety Planning

- **Construction**
  - Building materials
  - Fire-resistive ratings (minutes to hours)
  - Interior finishes (3 classes: A, B, & C)
- **Containing the fire**
  - Stair enclosures and fire walls
  - Separate building units or zones (control spread)
  - Fire doors
  - Smoke, heat and noxious gases control
  - Exits
- **Egress**
  - Two ways out, exit to safe area



Egress – Exit Route

- Continuous and unobstructed path from any point within a workplace
- Consists of three parts:
  - Exit access
  - Exit
  - Exit discharge
- Exit routes must be permanent
  - Unobstructed
- Well marked



Best Practices: Safety During a Fire…

- Stairs have a bar blocking the steps going down to indicate ground level fire egress
- Keep fire exits and stairwells free from any obstruction to allow for an easy exit during a fire emergency

Emergency Lighting

Proper storage of Flammables is an important part of Fire Safety

Limit quantities stored

Safety cans

Secondary Containment

Flammable storage cabinets, rooms or buildings

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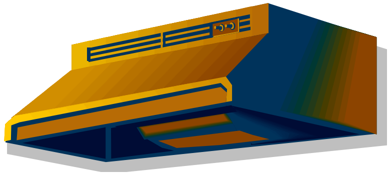
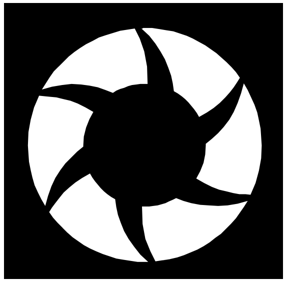
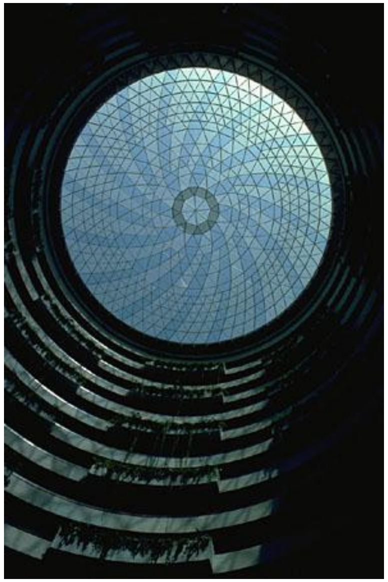
Ventilation

Always provide adequate ventilation to reduce the potential for ignition of flammable vapors.







Storage Containers

- Reduces fire risk
  - Limits oxygen
  - Encourage air circulation to remove heat
  - Limits access to ignition source.
- Containers should be tightly sealed when not in use

Storage Areas

Flammables should be stored in an approved cabinet in a cool, well ventilated area to avoid pressure buildup and vaporization

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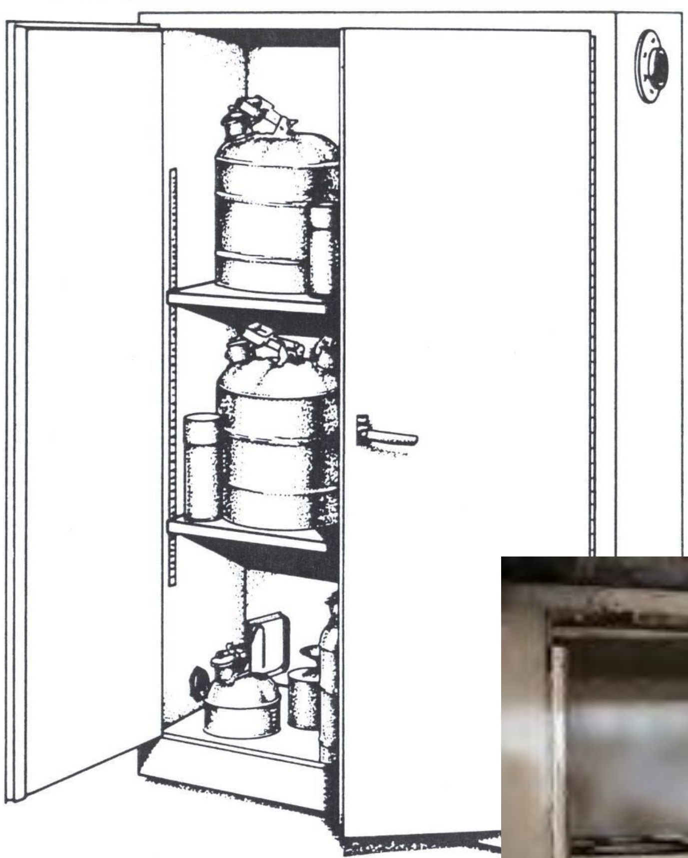
Flammable Storage Cabinets

Storage Cabinets

- Not more than 225 L of Class I and/or Class II liquids, or not more than 450 L of Class III liquids permitted in a cabinet.
- Must be conspicuously labeled, **"Flammable – Keep Fire Away"**
- Doors on metal cabinets must have a three-point lock (top, side, and bottom), and the door sill must be raised at least 5 cm above the bottom of the cabinet.

OSHA Office of Training and Education

Flammable Storage Cabinets



Static Electricity

- Some flammable liquids accumulate a static electric charge, which can release a spark that ignites the liquid
- Static electricity is generated by contact and separation of dissimilar materials:
  - Fluid flow through a pipe or into a tank
  - Agitation or mixing
  - Splash filling of containers

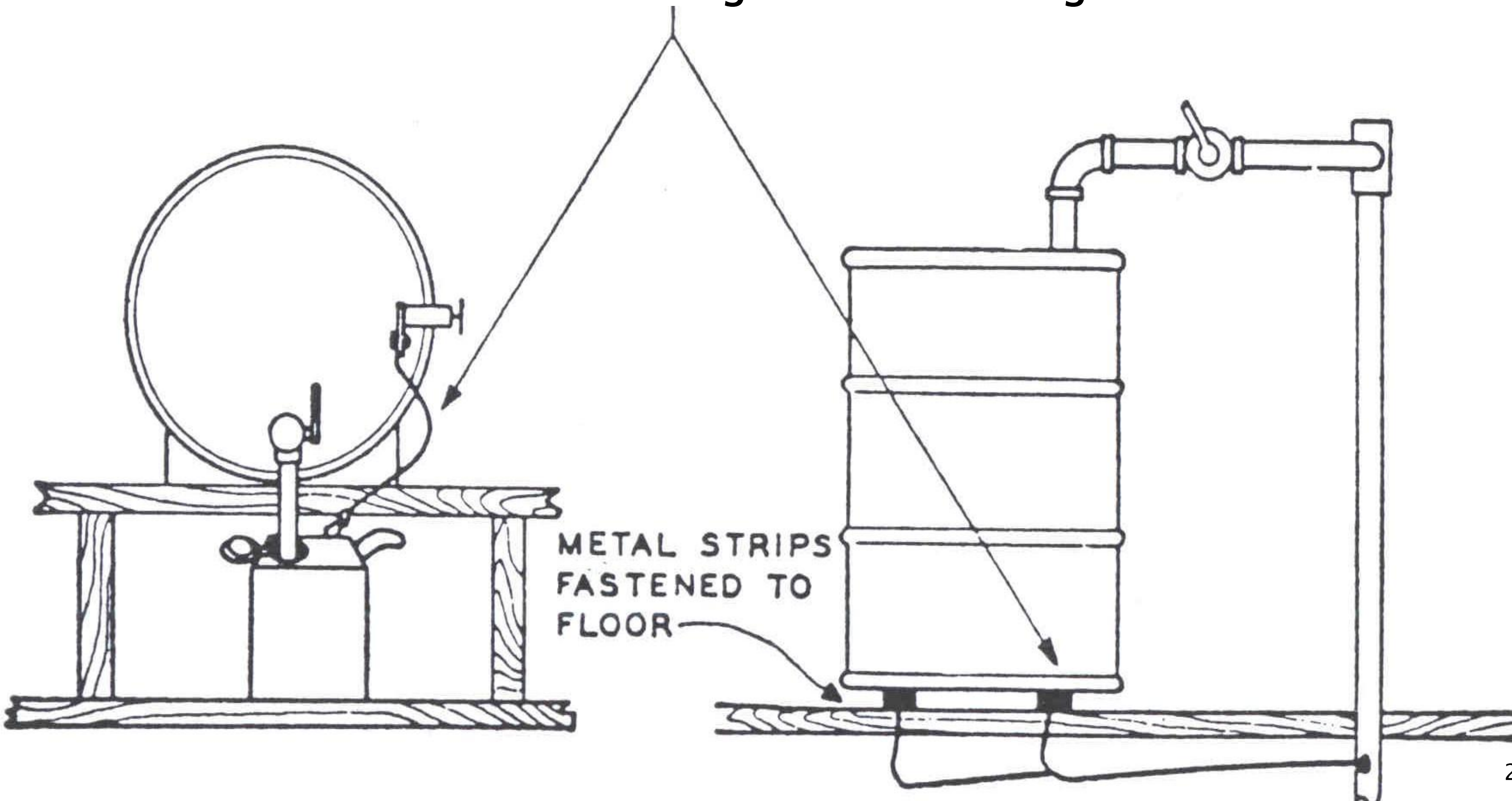
benzene toluene gasoline xylene

Transfer Techniques

- Bond containers
  - Containers are wired together before pouring
  - One container is connected to a good ground point to allow any charge to drain away safely
- Limit use of plastic containers to small volumes (< 4L)
  - No easy way to bond plastic containers

Control of Static

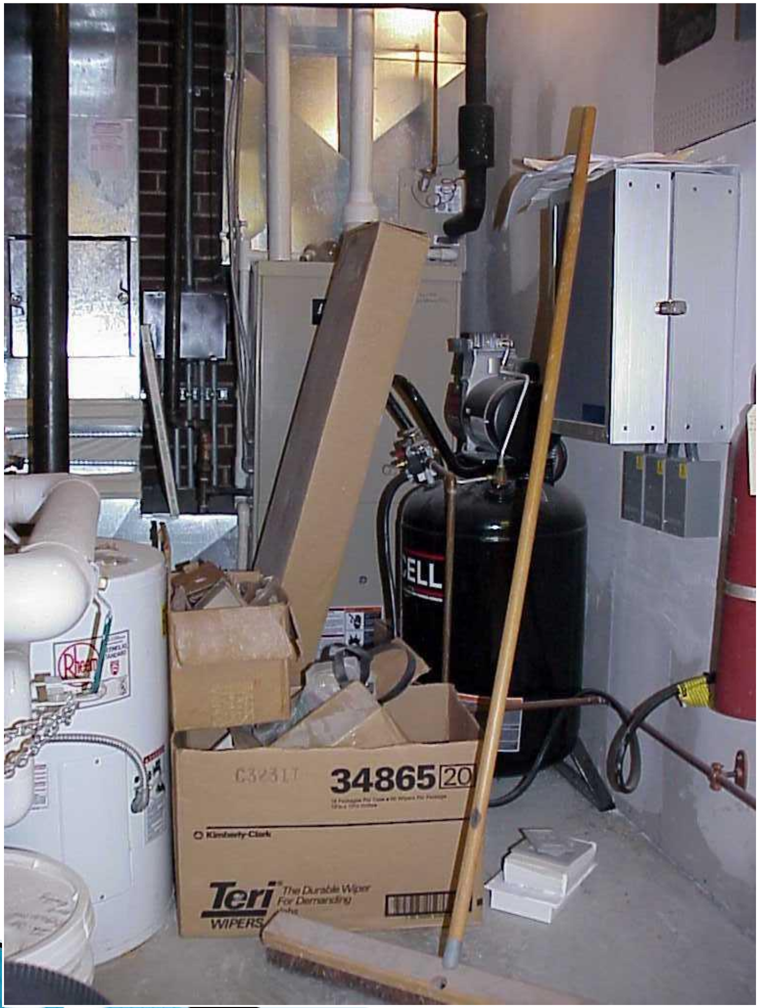
Bond wire necessary except where containers are inherently bonded together, or arrangement is such that fill stem is always in metallic contact with receiving container during transfer



Fire Prevention Inspections

- Minimize size of fires
  - Control storage of combustible and flammable materials
- Reduce possibility of a fire
  - Control ignition sources
- Ensure fire protection equipment is operational
  - Fire extinguishers not blocked
- Ensure exits are maintained
  - Don't block egress pathways
  - Don't prop open fire doors

Violations



Violations

<u>6-Way Multi-plug</u>

<u>Multi-plug</u>

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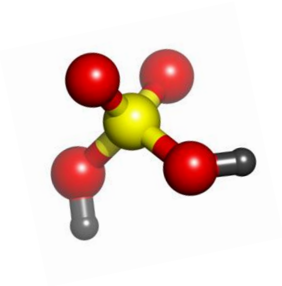
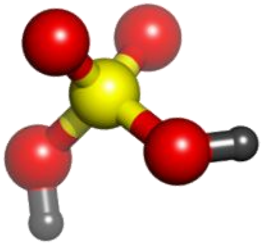
Any Questions?



Lunch



Chemical Reactivity Hazards

SAND No. 2012-1608C
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation,
a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000

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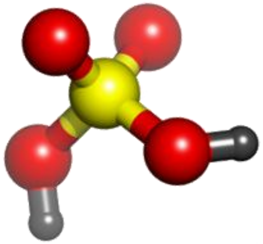
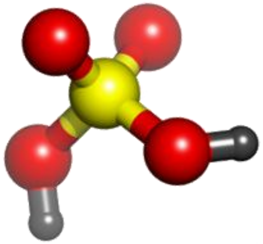
Sandia National Laboratories



Topics

- Definition of chemical reactivity hazard
- Some key reference materials
- A review of the chemical hazard diamond
- Steps to determine chemical hazards – an example
- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- Inherently safer systems



Key points of this module

- Identify the different types of chemical hazards.
- Awareness of the potential consequences.
- How to contain and control chemical hazards.
- A brief description of inherently safer systems.

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Key acronyms

DHS = Department of Homeland Security (USA)

CCPS = Center for Chemical Process Safety

CAMEO = computer-aided management of emergency operations

NIOSH = National Institutes of Occupational Safety and Health

NOAA = National Oceanic and Atmospheric Administration

AIChE = American Institute of Chemical Engineers

CSB = Chemical Safety Board

NFPA = National Fire Protection Association

WISER = Wireless Information System for Emergency Responders

US DOT = US Department of Transportation

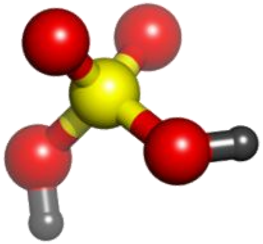
CHRIS = Chemical Hazard Response Information System

ASTM = American Society for Testing and Materials

DIERS = Design Institute for Emergency Relief Systems

SAChE = Safety and Chemical Engineering Education

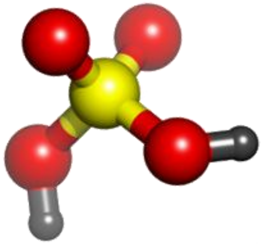
MIC = methyl isocyanate



Introduction

Chemical reactivity hazard:

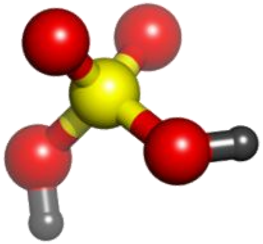
A situation with the potential for an <u>uncontrolled chemical reaction</u> that can result directly or indirectly in serious harm to people, property and/or the environment.



Introduction

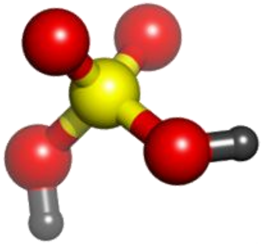
The worst process industry disasters worldwide have involved <u>uncontrolled chemical reactions</u>.

Examples?



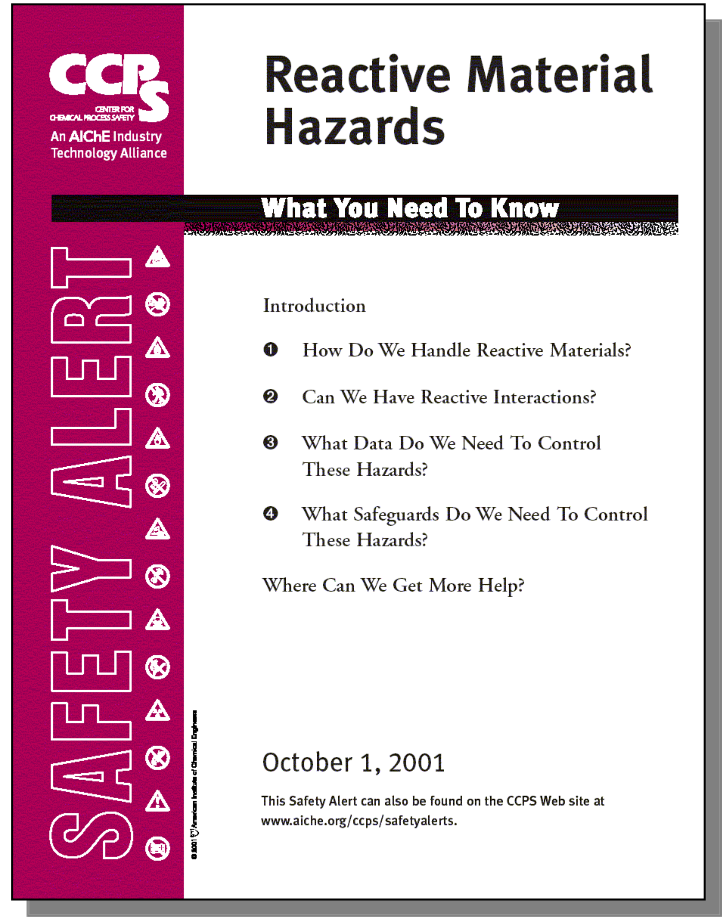
Introduction

- *Problem:* Chemical reactivity hazards are more difficult to anticipate and recognize than other types of process hazards.
- Inadequate recognition and evaluation of reactive chemical hazards was a causal factor in 60% of investigated reactive chemical incidents with known causes. (U.S. Chemical Safety Board Hazard Investigation)



Texts

CCPS Safety Alert 2001. ***Reactive Material Hazards: What You Need to Know.*** New York: AIChE. 10 pages.


CCPS
CENTER FOR CHEMICAL PROCESS SAFETY
An AIChE Industry Technology Alliance
SAFETY ALERT

Reactive Material Hazards

What You Need To Know

Introduction

1. How Do We Handle Reactive Materials?
2. Can We Have Reactive Interactions?
3. What Data Do We Need To Control These Hazards?
4. What Safeguards Do We Need To Control These Hazards?

Where Can We Get More Help?

October 1, 2001

This Safety Alert can also be found on the CCPS Web site at www.aiche.org/ccps/safetyalerts.

On course CD-ROM:

ccps-alert-reactive-materials.pdf

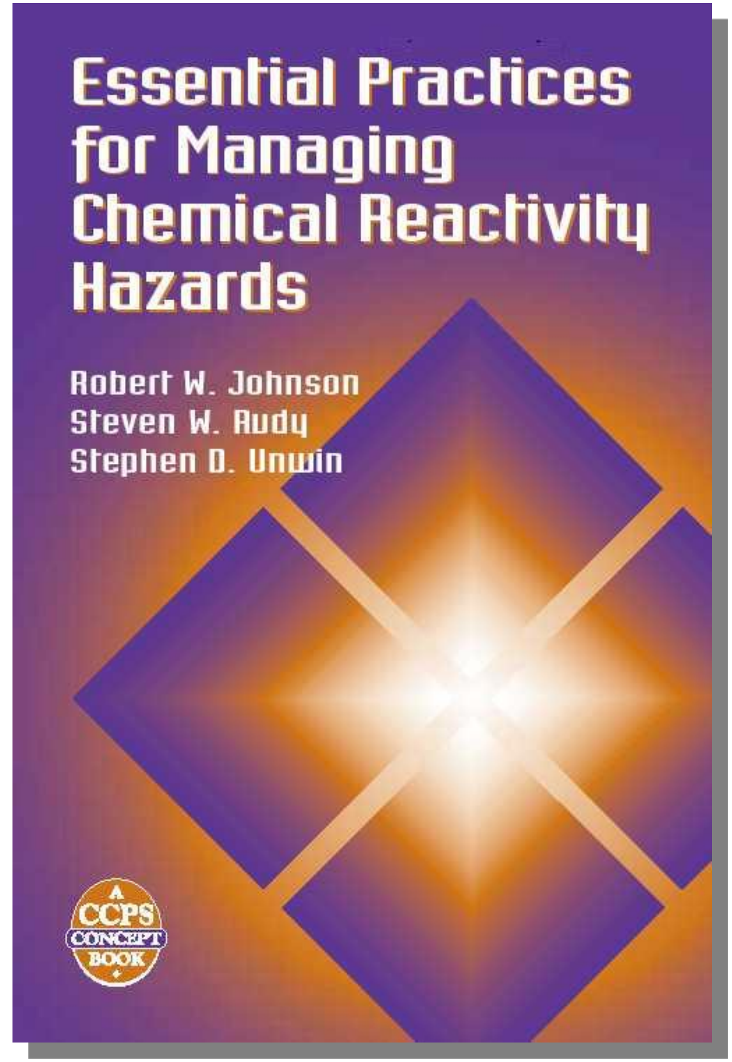
Texts

Johnson et al. 2003.

Essential Practices for Managing Chemical Reactivity Hazards.

New York: AIChE. 193 p.

Register for free access at
www.knovel.com/ccps



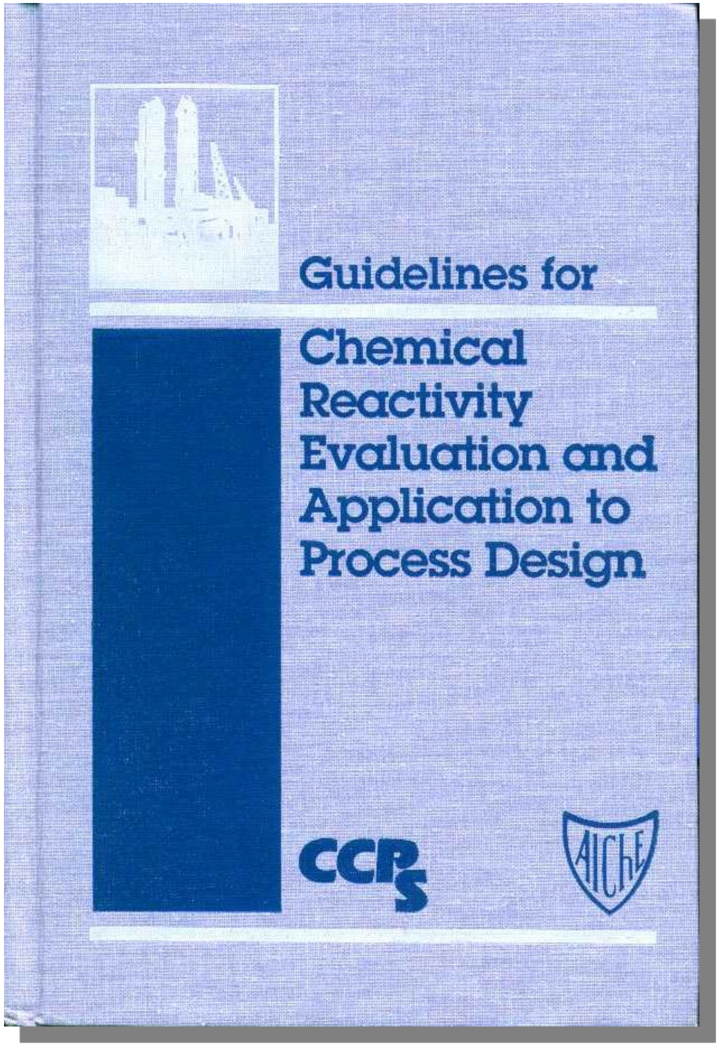
Texts

CCPS 1995.

Guidelines for Chemical Reactivity Evaluation and Application to Process Design.

New York: AIChE. 210 p.

AIChE members can access for free at www.knovel.com



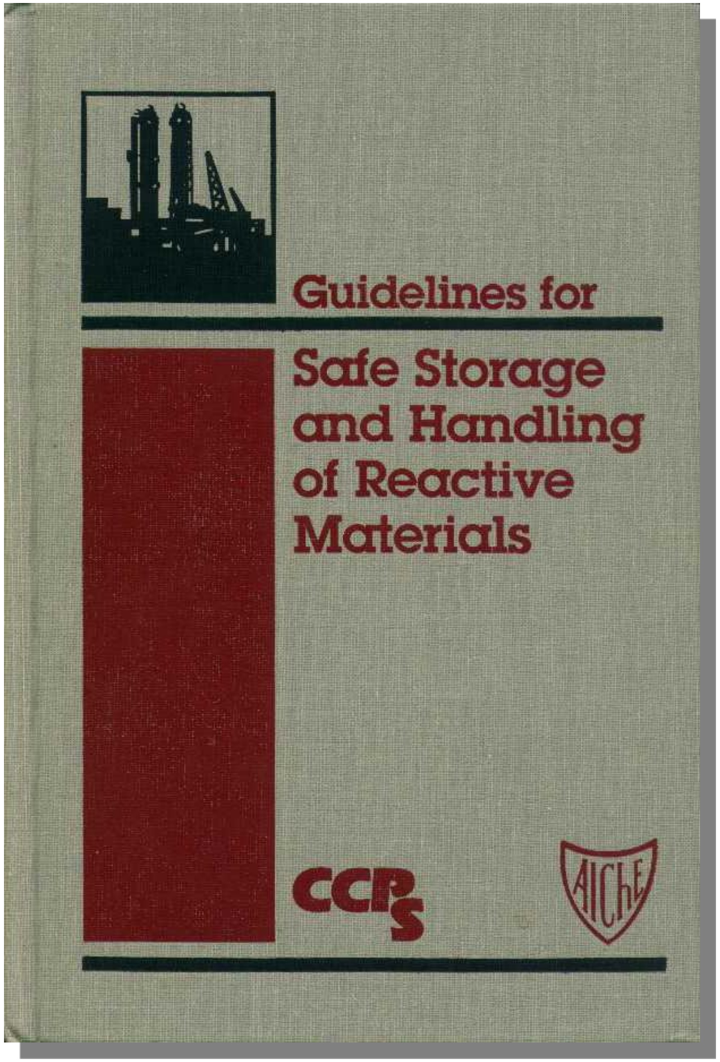
Texts

CCPS 1995.

Guidelines for Safe Storage and Handling of Reactive Materials.

New York: AIChE. 364 p.

AIChE members can access for free at www.knovel.com



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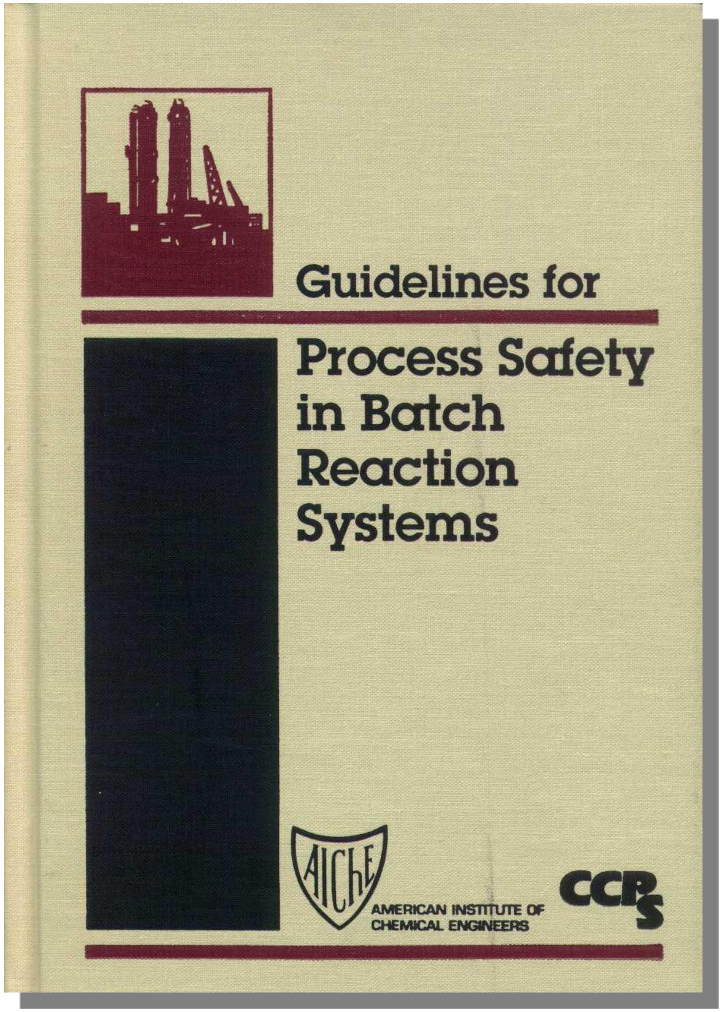
Texts

CCPS 1999.

Guidelines for Process Safety in Batch Reaction Systems.

New York: AIChE. 171 p.

Available from www.wiley.com



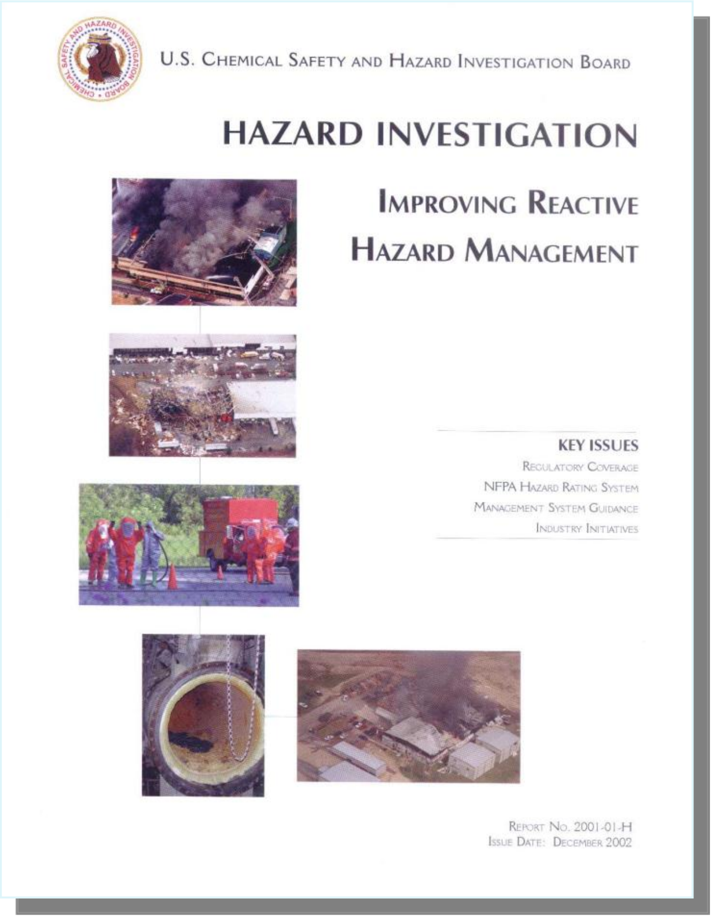
Texts

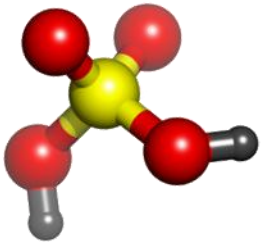
CSB 2002.

Improving Reactive Hazard Management.

Washington, D.C.: U.S. Chemical Safety and Hazard Investigation Board. 150 p.

Download for free at www.csb.gov

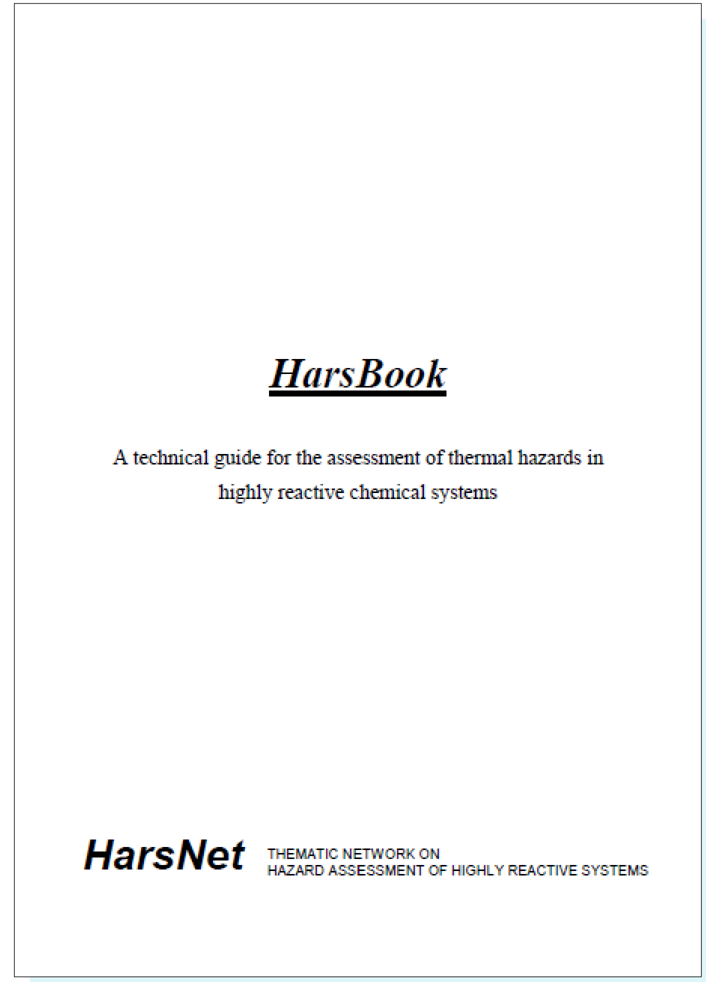




Texts

HarsBook: A technical guide for the assess-ment of thermal hazards in highly reactive chemical systems.

HarsNet Thematic Network on Hazard Assessment of Highly Reactive Systems. 143 p.

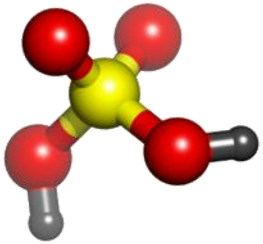


HarsBook

A technical guide for the assessment of thermal hazards in highly reactive chemical systems

HarsNet THEMATIC NETWORK ON HAZARD ASSESSMENT OF HIGHLY REACTIVE SYSTEMS

Download for free at www.harsnet.net/harsbook/harsbook_02.htm



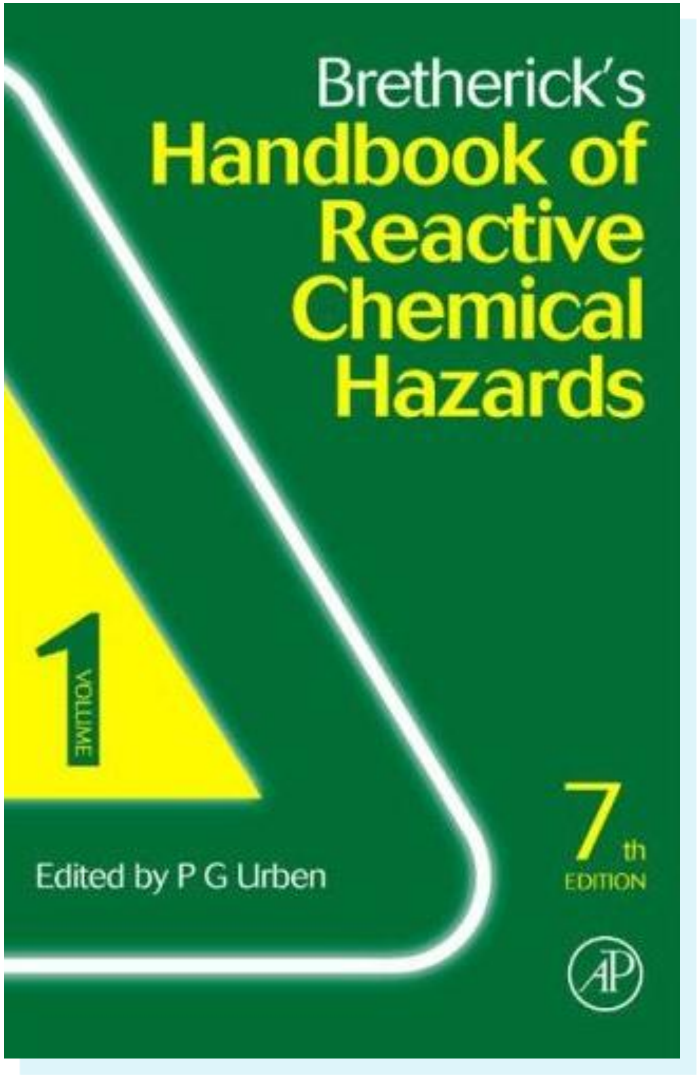
Texts

P.G. Urben (ed.) 2006.

Bretherick's Handbook of Reactive Chemical Hazards (2 vols).

Academic Press. 2680 p.

~US $500 from Amazon.com; also available electronically



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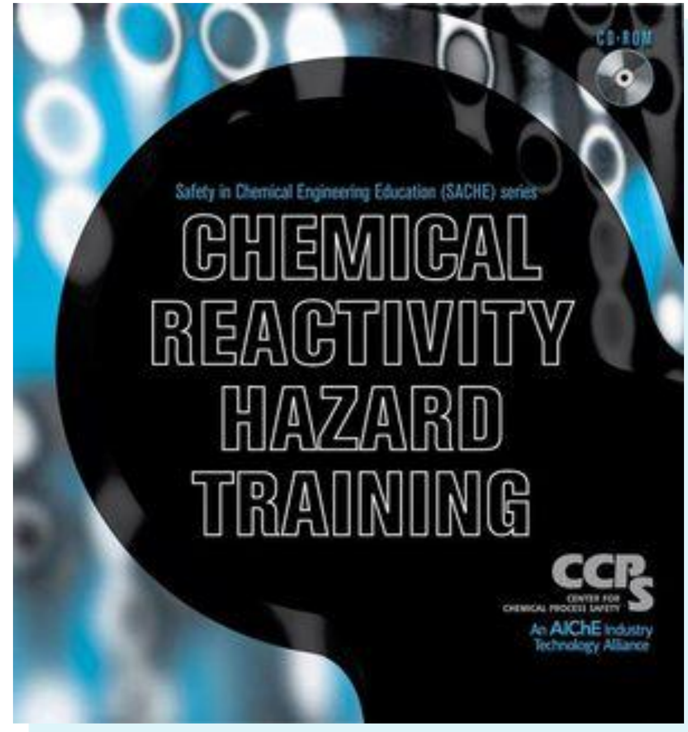
Software

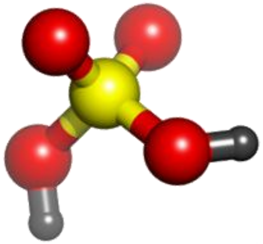
CCPS 2006.

Chemical Reactivity Training CD-ROM.

New York: AIChE.

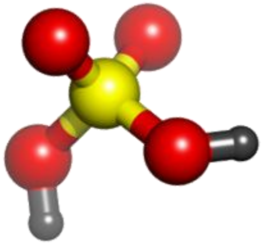
US $316 from wiley.com; free to all SAChE members (www.sache.org)





Pretest

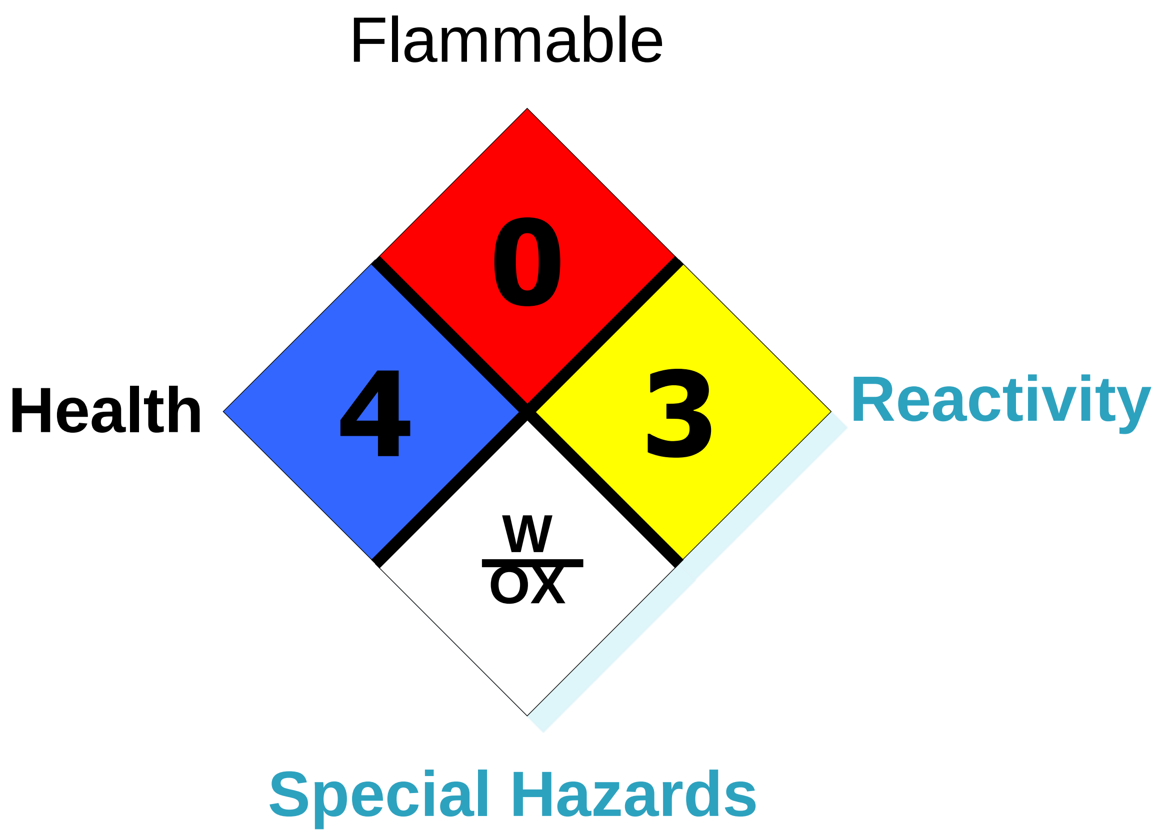
Q1 *On the National Fire Protection Agency (NFPA) 704 'diamond', which color(s) or position(s) are associated with* ***chemical reactivity hazards****?*

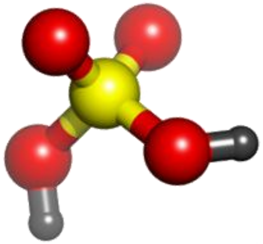


Pretest

A1

Number	Degree of Hazard
4	Extreme
3	Serious
2	Moderate
1	Slight
0	Minimal





Pretest

Q2

Your new research calls for the piloting of a process involving ***acetone cyanohydrin****.*

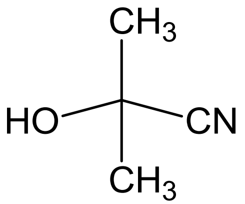
What should you do first?

Pretest

A2 *First, find out the inherent hazards of acetone cyanohydrin.*

C_4H_7NO

CAS No. 75-86-5



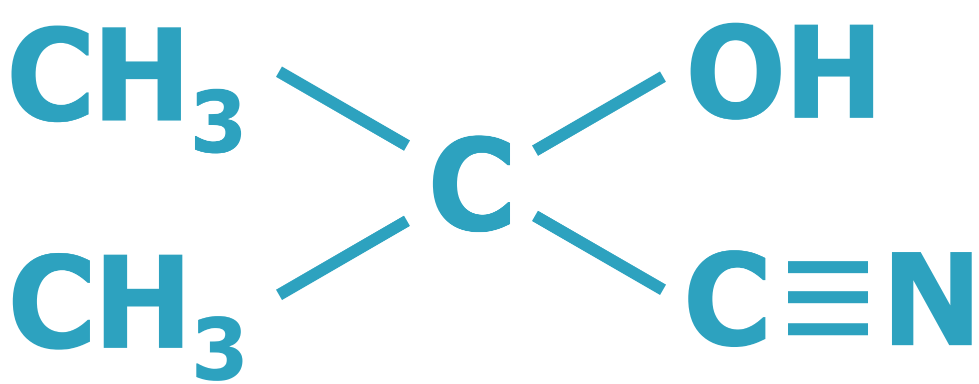
Pretest

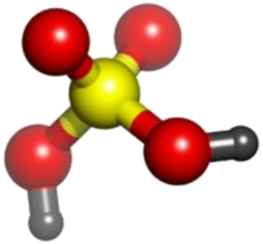
A2 *First, find out the inherent hazards of acetone cyanohydrin.*

$$\begin{matrix} CH_3 \diagdown \\ \quad\quad C=O \;+\; HCN \\ CH_3 \diagup \end{matrix}$$

Pretest

A2 *First, find out the inherent hazards of acetone cyanohydrin.*





Acetone cyanohydrin

NFPA 49

Severe health hazard; combustible; readily decomposes, producing HCN; not water-reactive or oxidizer; reacts with acids, alkalis, oxidizing materials, reducing agents

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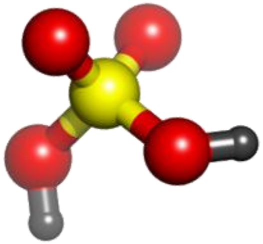


Acetone cyanohydrin

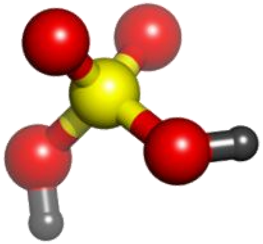
International Chemical Safety Card

Extremely toxic,

Class IIIB combustible,

unstable at elevated temperatures,

decomposes in water



Acetone cyanohydrin

WISER (wiser.nlm.nih.gov)

Highly Flammable: Easily ignited by heat, sparks or flames

Do Not Get Water, on spilled substance or inside containers

Wireless Information System for Emergency Responders

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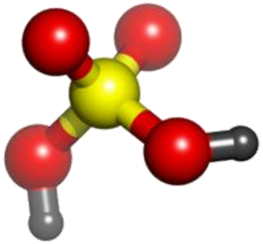
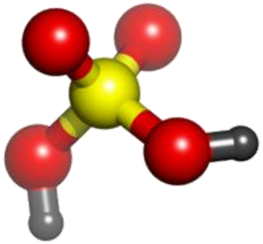


Acetone cyanohydrin

U.S. DOT

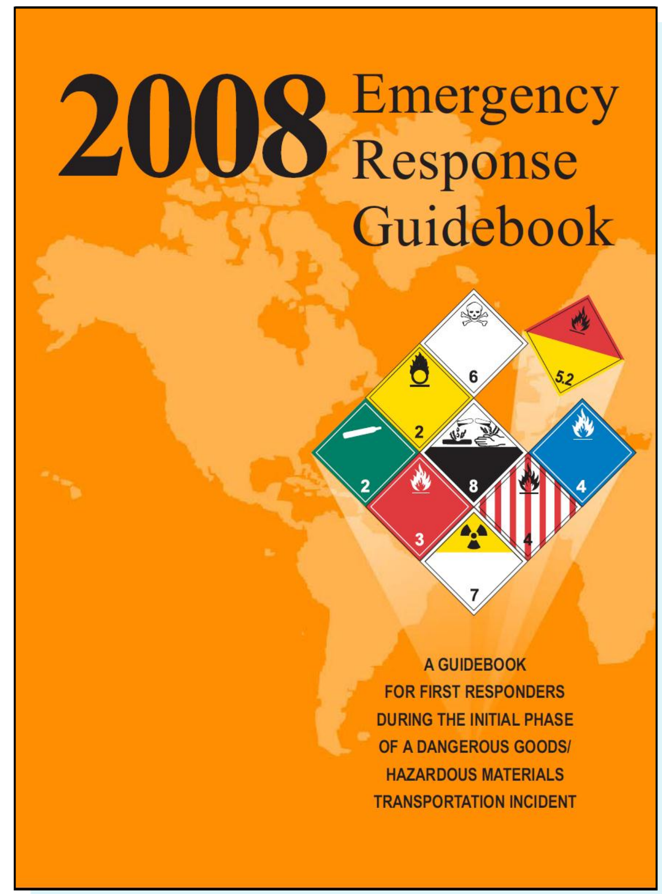
Class 6.1 Poisonous material

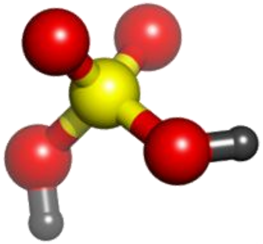


Acetone cyanohydrin

U.S. DOT Emergency Response Guidebook

“*A water-reactive material that produces large amounts of HCN when spilled in water”*





Acetone cyanohydrin

NOAA Chemical Reactivity Worksheet

Chemical Profile

Readily decomposes to acetone and poisonous hydrogen cyanide gas on contact with water, acids (sulfuric acid) or when exposed to heat. Should be kept cool and slightly acidic (pH 4-5) [Sax, 2nd ed., 1965, p. 388].

Slowly dissociates to acetone, a flammable liquid, and hydrogen cyanide, a flammable poisonous gas, under normal storage and transportation conditions. Rate of dissociation increased by contact with alkalis and/or heat.

Special Hazards

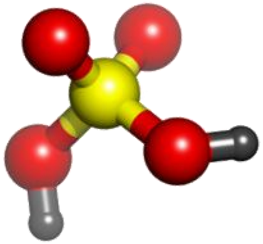
- *Water-reactive*
- *No rapid reaction with air*

Air and Water Reactions

Soluble in water. Readily decomposes on contact with water to form acetone and poisonous hydrogen cyanide.

General Description

A colorless liquid. Flash point 165°F. Lethal by inhalation and highly toxic or lethal by skin absorption. Density 7.8 lb / gal (less dense than water). Vapors heavier than air. Produces toxic oxides of nitrogen during combustion (© AAR, 1999).



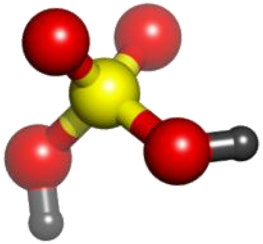
Acetone cyanohydrin

NIOSH Pocket Guide to Chemical Hazards

www.cdc.gov/niosh/npg/search.html

Incompatibilities and reactivities:
Sulfuric acid, caustics

Note: *Slowly decomposes to acetone and HCN at room temperatures; rate is accelerated by an increase in pH, water content, or temperature.*



Acetone cyanohydrin

CHRIS

U.S. COAST GUARD

Chemical Hazards Response Information System (CHRIS)

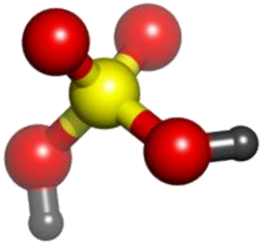
Click on the desired CHRIS Code to view the chemical sheet:

CHRIS Code	Chemical Name	Description
ACY	ACETONE CYANOHYDRIN	see below

Color:	Colorless
Odor:	Mild, almond odor.
Physical State Shipped:	Watery liquid
Characteristics In Water:	Floats and mixes with water. Poisonous vapor is produced.
IMO-UN Number:	6.1/1541
DOT ID Number:	1541
NFPA Hazard Classification:	Health Hazard (Blue) -
	Flammability (Red) -
	Reactivity (Yellow) -
	Special (White) -
View Synonyms	

cameochemicals.noaa.gov

CSP CHEMICAL SECURITY ENGAGEMENT PROGRAM



Acetone Cyanohydrin

CHRIS

4. FIRE HAZARDS

4.1 **Flash Point:** 165°F C.C.

4.2 **Flammable Limits in Air:** 2.2%-12%

4.3 **Fire Extinguishing Agents:** Water spray, dry chemical, alcohol foam, carbon dioxide

4.4 **Fire Extinguishing Agents Not to Be Used:** Not pertinent

4.5 **Special Hazards of Combustion Products:** Toxic hydrogen cyanide is generated when heated

4.6 **Behavior in Fire:** Not pertinent

4.7 **Auto Ignition Temperature:** 1270°F

4.8 **Electrical Hazards:** I, D

4.9 **Burning Rate:** Currently not available

4.10 **Adiabatic Flame Temperature:** Currently not available

4.11 **Stoichometric Air to Fuel Ratio:** Currently not available

4.12 **Flame Temperature:** Currently not available

4.13 **Combustion Molar Ratio (Reactant to Product):** Currently not available

4.14 **Minimum Oxygen Concentration for Combustion (MOCC):** Not listed

5. CHEMICAL REACTIVITY

5.1 **Reactivity with Water:** No reaction

5.2 **Reactivity with Common Materials:** No reaction

5.3 **Stability During Transport:** Stable

5.4 **Neutralizing Agents for Acids and Caustics:** Not pertinent

5.5 **Polymerization:** Not pertinent

5.6 **Inhibitor of Polymerization:** Not pertinent

7. SHIPPING INFORMATION

7.1 **Grades of Purity:** 98-99%

7.2 **Storage Temperature:** Ambient

7.3 **Inert Atmosphere:** No requirement

7.4 **Venting:** Pressure-vacuum

7.5 **IMO Pollution Category:** A

7.6 **Ship Type:** 2

7.7 **Barge Hull Type:** 1

8. HAZARD CLASSIFICATIONS

8.1 **49 CFR Category:** Poison

8.2 **49 CFR Class:** 6.1

8.3 **49 CFR Package Group:** I

8.4 **Marine Pollutant:** No

8.5 **NFPA Hazard Classification:**

Category	Classification
Health Hazard (Blue)..........	4
Flammability (Red).............	2
Instability (Yellow)............	2

8.6 **EPA Reportable Quantity:** 10

8.7 **EPA Pollution Category:** A

8.8 **RCRA Waste Number:** P069

8.9 **EPA FWPCA List:** Yes

9. PHYSICAL & CHEMICAL PROPERTIES

9.1 **Physical State at 15° C and 1 atm:** Liquid

9.2 **Molecular Weight:** 85.11

9.3 **Boiling Point at 1 atm:** Decomposes (~74.4C)

9.4 **Freezing Point:** –5.8°F = –21°C = 252°K

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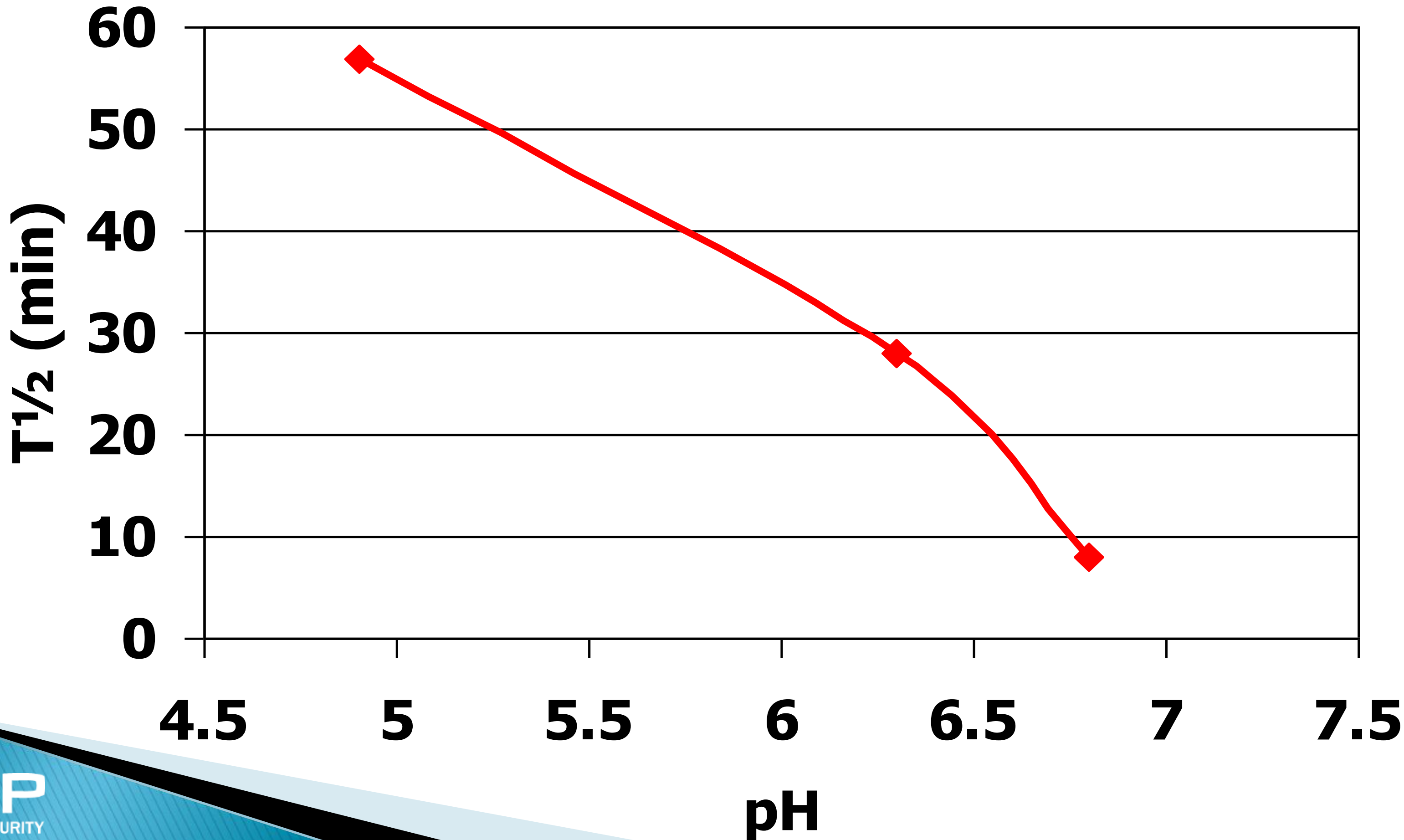
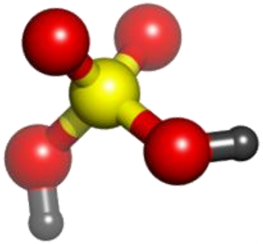
Acetone cyanohydrin

SIDS: Stability in Water

(OECD Screening Information Dataset)

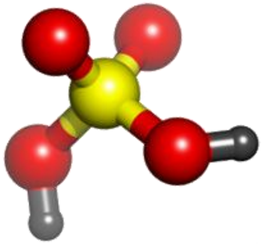




Acetone cyanohydrin

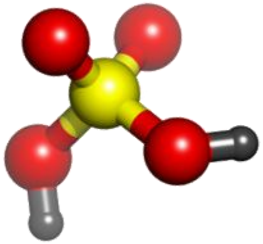
Conclusions:

- Extremely toxic; must keep contained and avoid all contact
- Combustible; must avoid flame, ignition
- Dissociates to produce highly toxic and flammable gases; dissociation increases with heat, moisture, alkalinity
- Must prevent spills into drains, etc.
- Must avoid incompatible materials



Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- Inherently safer systems



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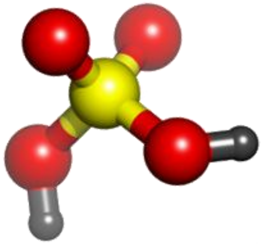

- Intentional chemical reactions
- Unintentional reactions
  - **Materials reactive with common substances**
    - Spontaneously combustible
    - Peroxide-forming
    - Water-reactive
    - Oxidizing
  - **Self-reactive materials**
    - Polymerizing
    - Decomposing
    - Rearranging
  - **Reactive interactions**
    - Incompatibilities
    - Abnormal conditions

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<table>
<tr><th>Main Category</th><th>Subcategory</th><th>Adjective</th><th colspan="2">Noun</th></tr>
<tr><td rowspan="7">READILY SELF-REACTS with energy input such as by shock, pressure, or temperature (UNSTABLE MATERIALS)</td><td colspan="2">POLYMERIZES</td><td colspan="2">MONOMERS</td></tr>
<tr><td rowspan="4">DECOMPOSES</td><td>SHOCK-SENSITIVE</td><td>EXPLOSIVES</td><td rowspan="4">Toxic / flammable decomposition products</td></tr>
<tr><td rowspan="2">THERMALLY SENSITIVE (Decomposes upon heating; may require pressure/confinement)</td><td>EXPLOSIVES</td></tr>
<tr><td>Other unstable or thermally sensitive materials</td></tr>
<tr><td colspan="2">SENSITIVE TO OTHER STIMULUS (e.g. friction, spark, light, pressure)</td></tr>
<tr><td>REARRANGES</td><td colspan="3">ISOMERIZING / TAUTOMERIZING / DISPROPORTIONATING</td></tr>
<tr><td colspan="4">CONDENSES</td></tr>
<tr><td rowspan="8">READILY REACTS WITH COMMON ENVIRONMENTAL SUBSTANCES</td><td colspan="4">REACTS WITH ATMOSPHERIC NITROGEN</td></tr>
<tr><td rowspan="3">REACTS WITH ATMOSPHERIC OXYGEN</td><td colspan="3">SPONTANEOUSLY COMBUSTIBLE (including hypergolic, pyrophoric)</td></tr>
<tr><td colspan="3">FLAMMABLE / COMBUSTIBLE (includes explosible dusts; usually treated separately from reactives)</td></tr>
<tr><td colspan="3">PEROXIDE FORMING</td></tr>
<tr><td>REACTS WITH WATER</td><td>WATER REACTIVE (DANGEROUS WHEN WET)</td><td colspan="2">Rate of reaction can vary from slow to explosively violent</td></tr>
<tr><td rowspan="2">REACTS WITH ORDINARY COMBUSTIBLES</td><td rowspan="2">OXIDIZING</td><td colspan="2">ORGANIC PEROXIDES</td></tr>
<tr><td colspan="2">Other OXIDIZERS</td></tr>
<tr><td colspan="4">REACTS WITH METALS</td></tr>
<tr><td rowspan="3">READILY REACTS WITH OTHER CHEMICALS (INCOMPATIBLE MATERIALS)</td><td colspan="4">REACTS WITH ACIDS</td></tr>
<tr><td colspan="4">REACTS WITH BASES</td></tr>
<tr><td colspan="4">REACTS WITH HYDROGEN</td></tr>
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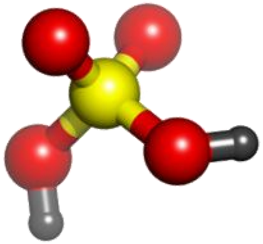
(etc.)



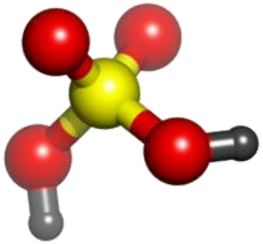
Chemical reactivity hazards

Some chemicals have more than one reactive property.

R–O–O–R

For example, **organic peroxides** can be any or all of:

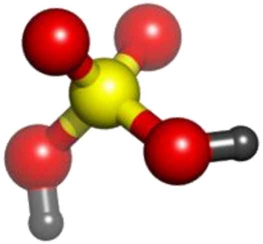
- **Oxidizing**
- **Decomposing** (shock-sensitive / thermally unstable)
- **Flammable** or **combustible**
- **Interacting** (incompatible with many other chemicals)



Chemical reactivity hazards

Some types of molecular structures tend to increase chemical reactivity, such as:

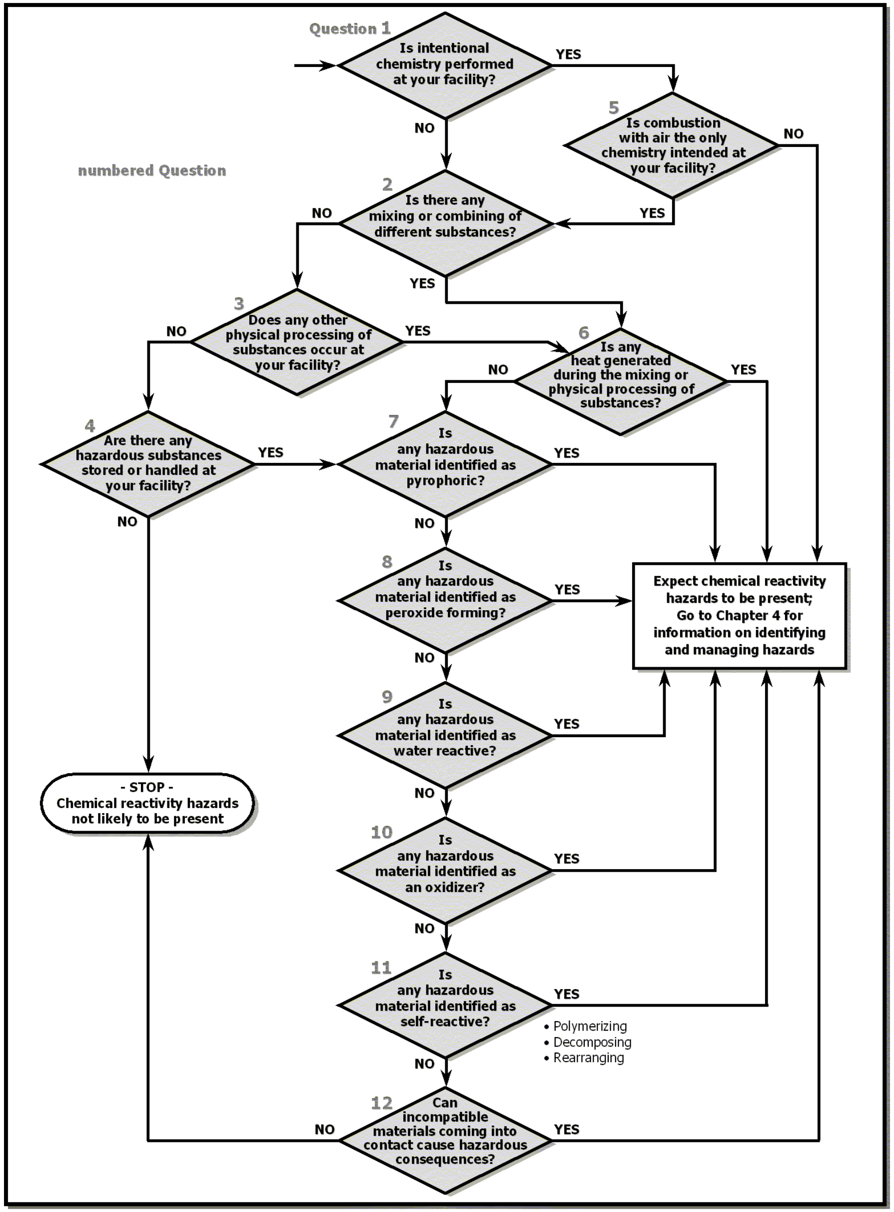
- Carbon-carbon double bonds not in benzene rings (ethylene, styrene...)
- Carbon-carbon triple bonds (e.g., acetylene)
- Nitrogen-containing compounds (NO_2 groups, adjacent N atoms ...)
- Oxygen-oxygen bonds (peroxides, hydroperoxides, ozonides)
- Ring compounds with only 3 or 4 atoms (e.g., ethylene oxide)
- Metal- and halogen-containing complexes (metal fulminates; halites, halates; etc.)



Preliminary Screen for Chemical Reactivity Hazards

Summary Flowchart

Source: **Johnson et al. 2003**



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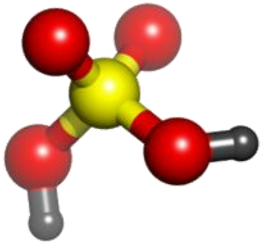

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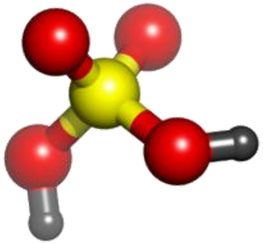
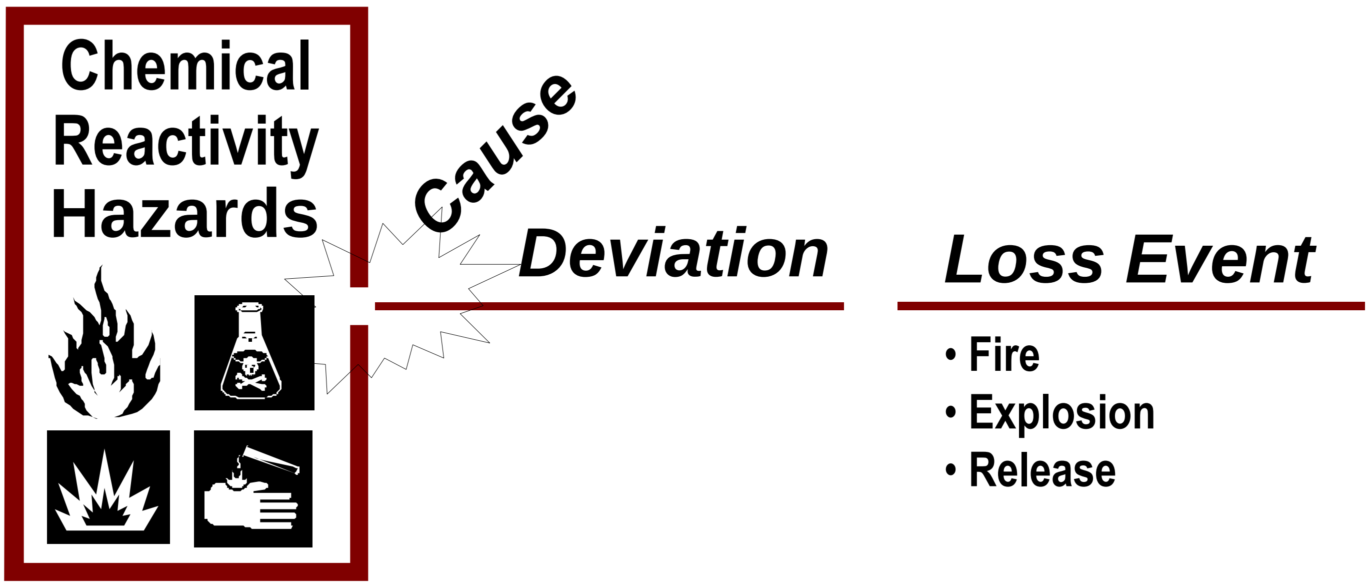
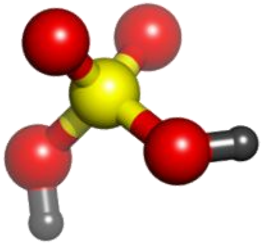


Normal situation

- Reactive materials contained
- Reactive interactions (incompatibilities) avoided
- Intended reactions controlled

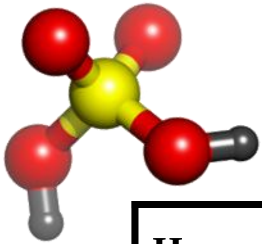
Abnormal situation





Loss events associated with reactivity hazards

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Intentional Chemistry	***Containment rupture explosion*** (uncontrolled reaction resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Fire*** (e.g., excess heating or loss of cooling in unconfined configuration allows autoignition temperature to be attained) ***Toxic reaction products release*** (e.g., off-gas treatment system fails)
Spontaneously Combustible Materials	***Containment rupture explosion*** (self-ignition of vapor, dust or mist inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Fire*** (e.g., self-ignition of flash fire, jet fire, pool fire, pile fire, or building fire) ***Toxic combustion gases release***
Peroxide Formers	***Condensed-phase explosion*** (e.g., explosive decomposition of unstable peroxide initiated by heat, friction, spark, or mechanical shock) ***Fire*** (e.g., follow-on effects from condensed-phase explosion, such as flammable liquid containment rupture and ignition)



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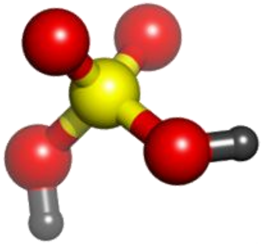
	ture explosion (self-ignition of vapor, dust or mist ly relieved vessel or enclosure that is incapable of k pressure) nition of flash fire, jet fire, pool fire, pile fire, or ***n gases release***
Formers	***se explosion*** (e.g., explosive decomposition of unstable peroxide initiated by heat, friction, spark, or mechanical shock) ***Fire*** (e.g., follow-on effects from condensed-phase explosion, such as flammable liquid containment rupture and ignition)

T-2 Incident

Jacksonville, Florida

December 2007



Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Water-Reactive Materials	***Explosively violent reaction*** (e.g., reaction of sodium with water) ***Containment rupture explosion*** (reaction with water resulting in liquid/vapor heating or gas generation inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure, or flammable vapors generated by reaction with water ignited inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Flash fire*** (e.g., ignition of unconfined flammable vapors generated by reaction with water) ***Toxic vapor release*** (toxic vapors generated by reaction with water, or decomposition reaction initiated by heat of reaction with water)
Oxidizers	***Fire*** (initiated or accelerated by presence of oxidizer) ***Condensed-phase explosion*** (initiation of detonable mixture of oxidizer with reducing substance) ***Containment rupture explosion*** (ignition or spontaneous ignition of oxidation reaction inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic combustion gases release*** • Note that many oxidizers are subject to decomposition, so also have possible Self-Reactive Material consequences

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
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Oxidizers	***Fire*** (initiated or ac ed by presence of oxidizer) ***Condensed-p*** able mixture of oxidizer with ***Containmen*** ntaneous ignition of oxidation rea essel or enclosure that is incapable ***Toxic combu*** • Note that m position, so also have ssible Self-

Bhopal
India
December 1984

Hazard Type	Typical Uncontrolled Chemical Reaction Consequences
Self-Reactive Materials (Polymerizing, Decomposing, Rearranging)	***Condensed-phase explosion*** (e.g., heat, friction, spark, or mechanical shock initiation of decomposition proceeding at detonation velocity) ***Containment rupture explosion*** (e.g., by self-reaction resulting in liquid/vapor heating, gas generation, or evolution and ignition of flammable vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic decomposition products or heat from self-reaction resulting in vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Pile fire*** (e.g., by self-heating to autoignition temperature)
Incompatible Materials	***Condensed-phase explosion*** (e.g., by initiation of detonable mixture) ***Containment rupture explosion*** (e.g., by liquid/vapor heating, gas generation, or evolution and ignition of flammable vapors inside inadequately relieved vessel or enclosure that is incapable of withstanding peak pressure) ***Toxic vapor release*** (e.g., from toxic reaction products or from heating and vaporization of toxic component) ***Flash fire*** (e.g., by ignition of flammable off-gases) ***Hazardous material spill*** (e.g., loss of containment due to reaction with wrong material of construction)

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Toulouse
France
September 2001

Incompatible materials

How would you define "chemical incompatibility"?

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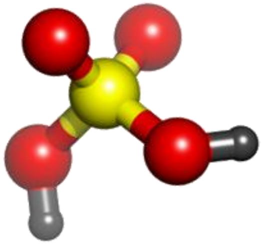


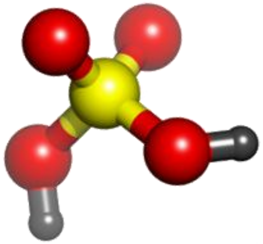
ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

- Define scenario
- Define incompatibility
- Compile chart

www.astm.org

CHEMICAL SECURITY ENGAGEMENT PROGRAM



ASTM E 2012

"Standard Guide for the Preparation of a Binary Chemical Compatibility Chart"

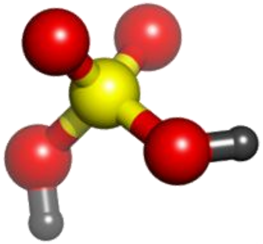
- Define scenario
  - Quantities
  - Temperatures
  - Confinement
  - Atmosphere (air, nitrogen, inerted)
  - Contact time

ASTM E 2012

“Standard Guide for the Preparation of a Binary Chemical Compatibility Chart”

- Define scenario
- Define incompatibility

“In a general sense, chemical incompatibility implies that there may be undesirable consequences of mixing these materials at a macroscopic scale. These consequences might be, in a worst case, a fast chemical reaction or an explosion, a release of toxic gas, or, in a less severe case, an undesirable temperature rise that might take the mixture above its flash point or cause an unacceptable pressure increase in the system…. Consequently, <u>a working definition of incompatibility needs to be formulated before compatibility judgments can be effectively and accurately made</u>.”



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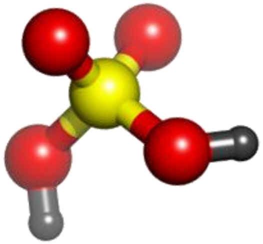
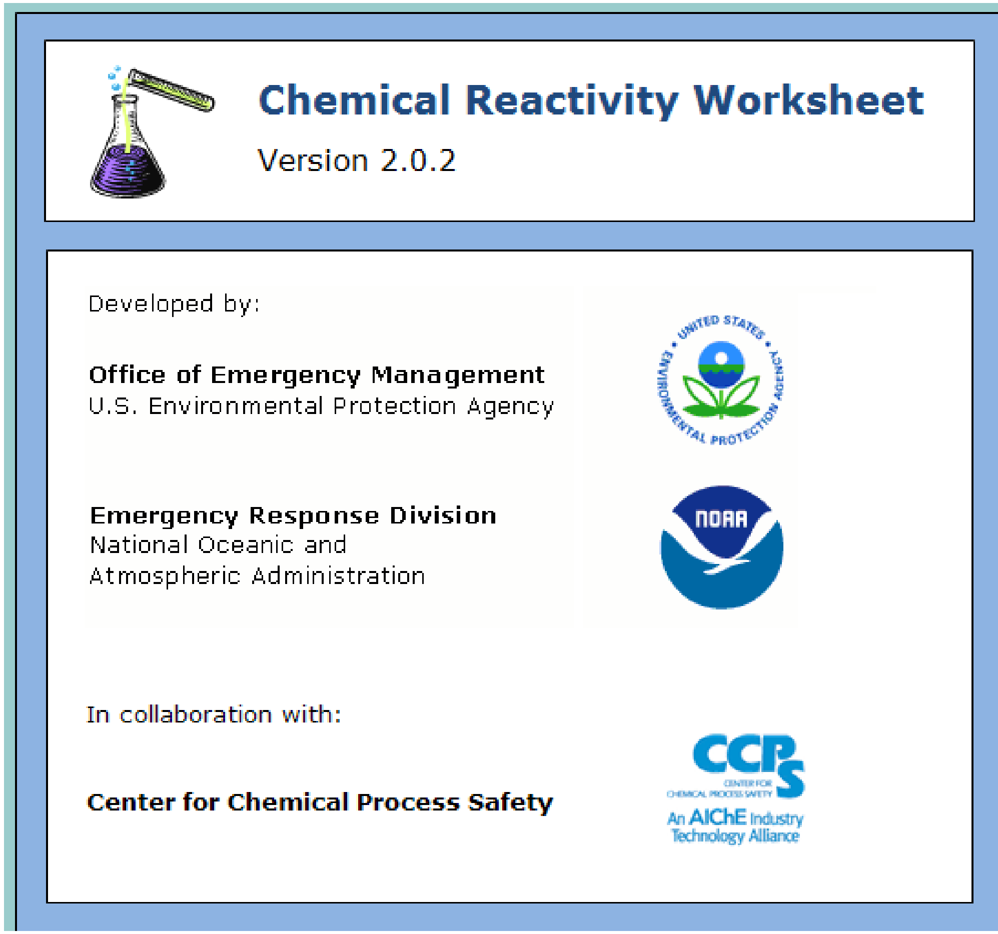


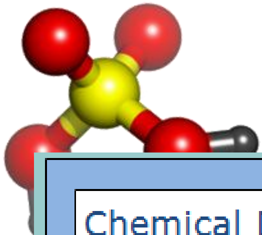
NOAA Chemical Reactivity Worksheet

response.restoration.noaa.gov/crw

The NOAA Chemical Reactivity Worksheet predicts the results of mixing any binary combination of the 6,000+ chemicals in the CAMEO database, including many common mixtures and solutions.

For each substance, a general description and chemical profile are given, along with special hazards such as air and water reactivity.





CRW data - Sodium hydrosulfite

Chemical Datasheet

General Info | **Reactivity** | **Synonyms**

Chemical Name: SODIUM HYDROSULFITE

Chemical Formula: Na2S2O4

CAS Number	UN/NA Number	USCG CHRIS CODE	DOT Hazard Label	DOT Hazard Class	Reactive Group Numbers
7775-14-6	1384		SPONTANEOUSLY COMBUSTIBLE		45

General Description

Sodium dithionite is a whitish to light yellow crystalline solid having a sulfur dioxide-like odor. It spontaneously heats on contact with air and moisture. This heat may be sufficient to ignite surrounding combustible materials. It is soluble in water. Under prolonged exposure to fire or intense heat containers of this material may violently rupture. It is used in dyeing and to bleach paper pulp.

Special Hazards

Strong Reducing Agent; Water-Reactive; Air-Reactive

Add Chemical to Worksheet

Sodium hydrosulfite + ethylene glycol

Reactivity Worksheet

Begin by searching for a chemical to add to the mixture. Return here to add water, reactive groups, and custom chemicals.

Reactivity Mixture

Chemical Name — 2 chemical(s) and/or reactive group(s) in mixture	Reactive Hazard Numbers	Reactive Group Numbers
ETHYLENE GLYCOL		4
SODIUM HYDROSULFITE	105, 107, 108	45

Remove All | Remove Selected Chemical | Add Custom Chemicals | Add Reactive Group | Add Water

Predicted Hazards | **Mixture Documentation** (for the reactive groups of the items in the mixture)

1) SODIUM HYDROSULFITE mixed with
2) ETHYLENE GLYCOL
- Reaction proceeds with explosive violence and/or forms explosive products
- May become highly flammable or may initiate a fire, especially if other combustible materials are present
- Combination liberates gaseous products, at least one of which is flammable. May cause pressurization
- Exothermic reaction. May generate heat and/or cause pressurization

Possible Gases:
Hydrogen
Hydrocarbons

To print hazards or documentation: Copy all text in the field above and paste into a word processor program, format as desired, then print.

Save This Mixture | Predict Hazards | Show Saved Mixtures | Preview Report | Show Compatibility Chart

CHEMICAL SECURITY ENGAGEMENT PROGRAM

Sodium hydrosulfite + ethylene glycol

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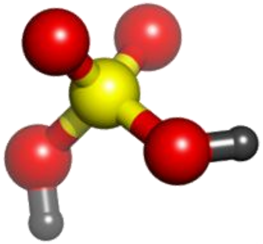
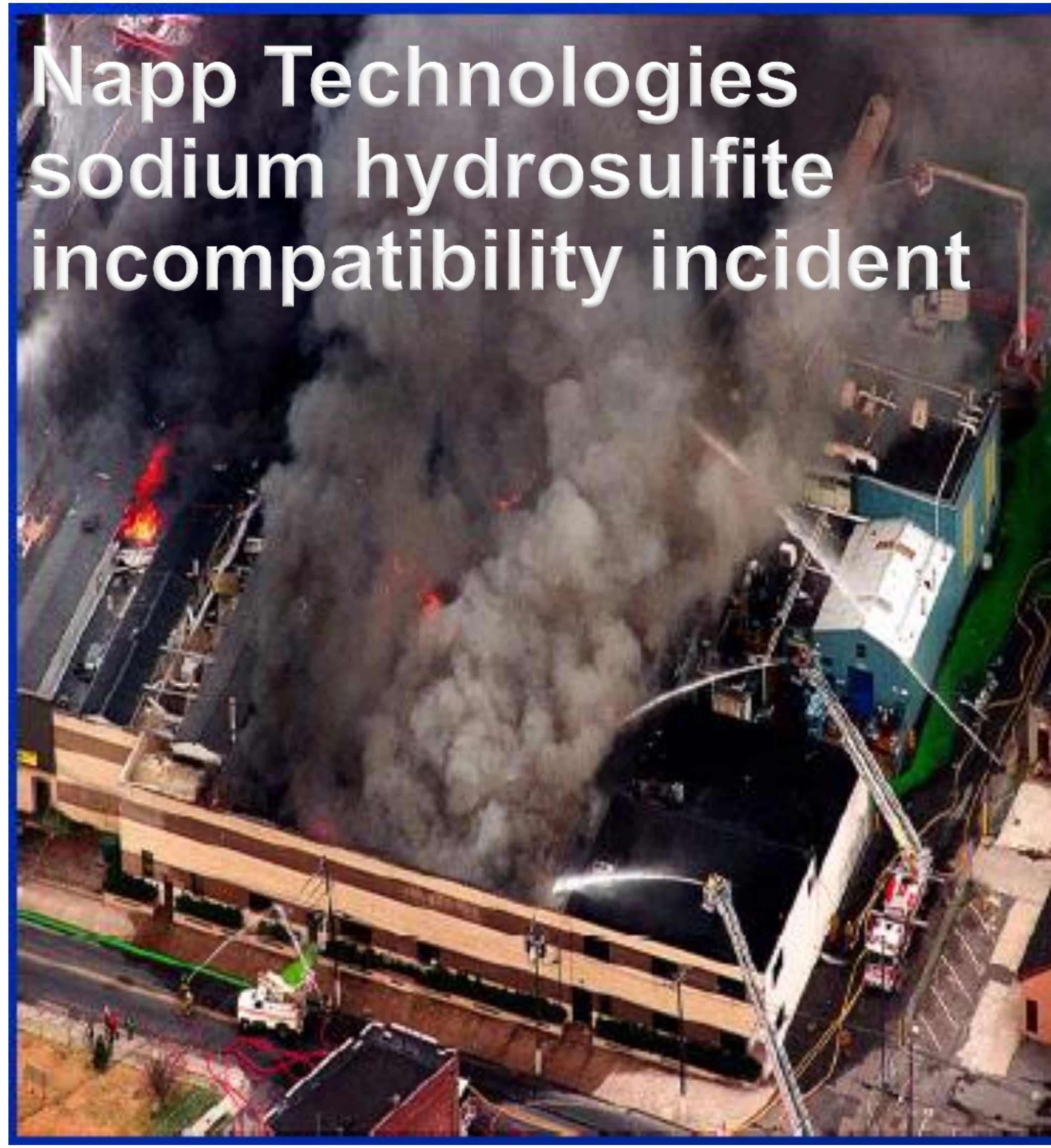
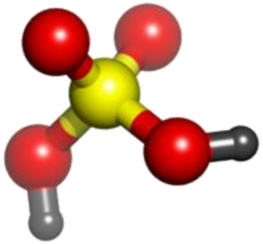


April 21, 1995

- 5 worker fatalities
- ~300 evacuated
- Facility destroyed
- Surrounding businesses damaged



Ed Hill, The Bergen Record



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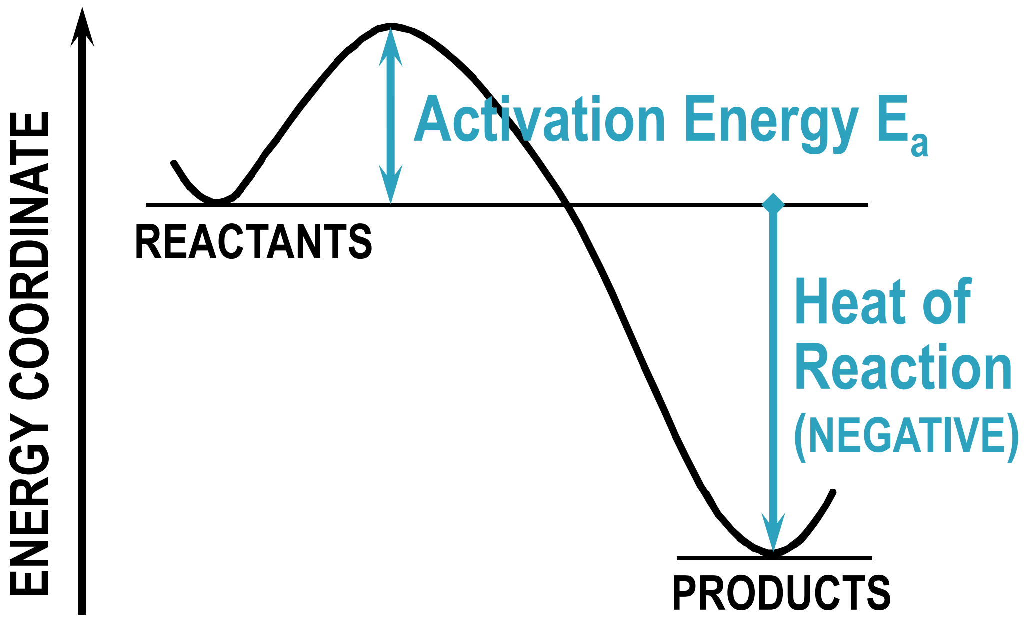
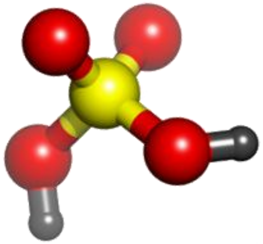
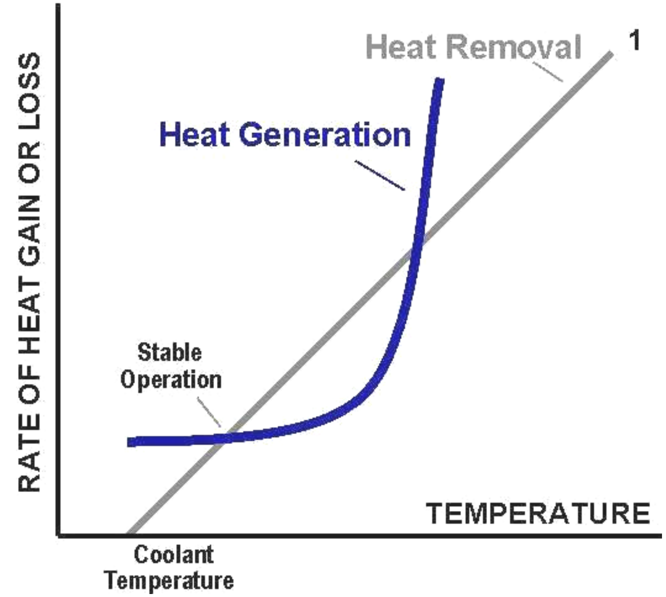
Chemical reactivity hazards

Energy diagram for exothermic reaction:



- Lower activation energy barrier ⮙ faster reaction
- Larger heat of reaction ⮙ more energy released





Key term to understand:

"Runaway reaction"

For an exothermic chemical reaction: FIRST-ORDER KINETICS

- Reaction rate is exponential *f* (temperature) $k = A\ e^{(-Ea/RT)}$
- If reaction temperature increases, rate increases and more heat is released by exothermic reaction
- If this heat is not removed, it further increases the reaction rate
- Then even more heat is released, etc.
- Temperature can rise hundreds of °C per minute!
- Pressure is generated by product gases and/or liquid boiling
- Reactor may rupture if pressure not safely vented

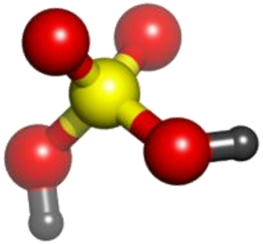
U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

T2 LABORATORIES, INC.

RUNAWAY REACTION

(Four Killed, 32 Injured)



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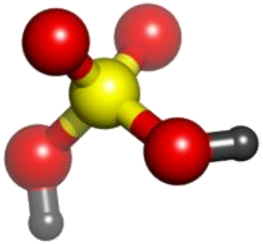


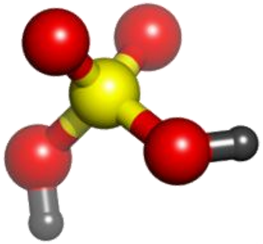
Foresee, Avoid, Control

- Anticipate chemical reactivity hazards
- Identify all reactive materials and all possible reactive interactions
- Do whatever it takes to fully understand intended and unintended reactions
  - Boundaries of safe operation
  - Calculations, literature, testing, experts
- Design and operate to avoid unintended reactions and control intended reactions

Safe operation

(with respect to chemical reactivity hazards)

- Contain and control all chemical reactivity hazards throughout entire facility lifetime
- ***OR*** Reduce hazards or design safeguards such that even if hazard containment or control were lost, no injuries, property damage, environmental damage or business interruption would occur
- ***OR*** Eliminate chemical reactivity hazards



Managing chemical reactivity hazards

- More effort is required to identify and characterize the reactivity hazards
- This may require small-scale testing
- See flowchart on next page

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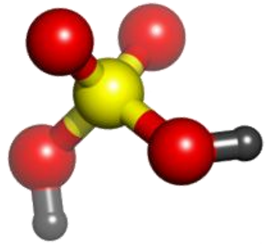
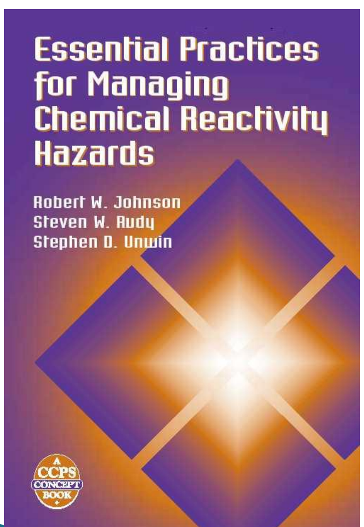
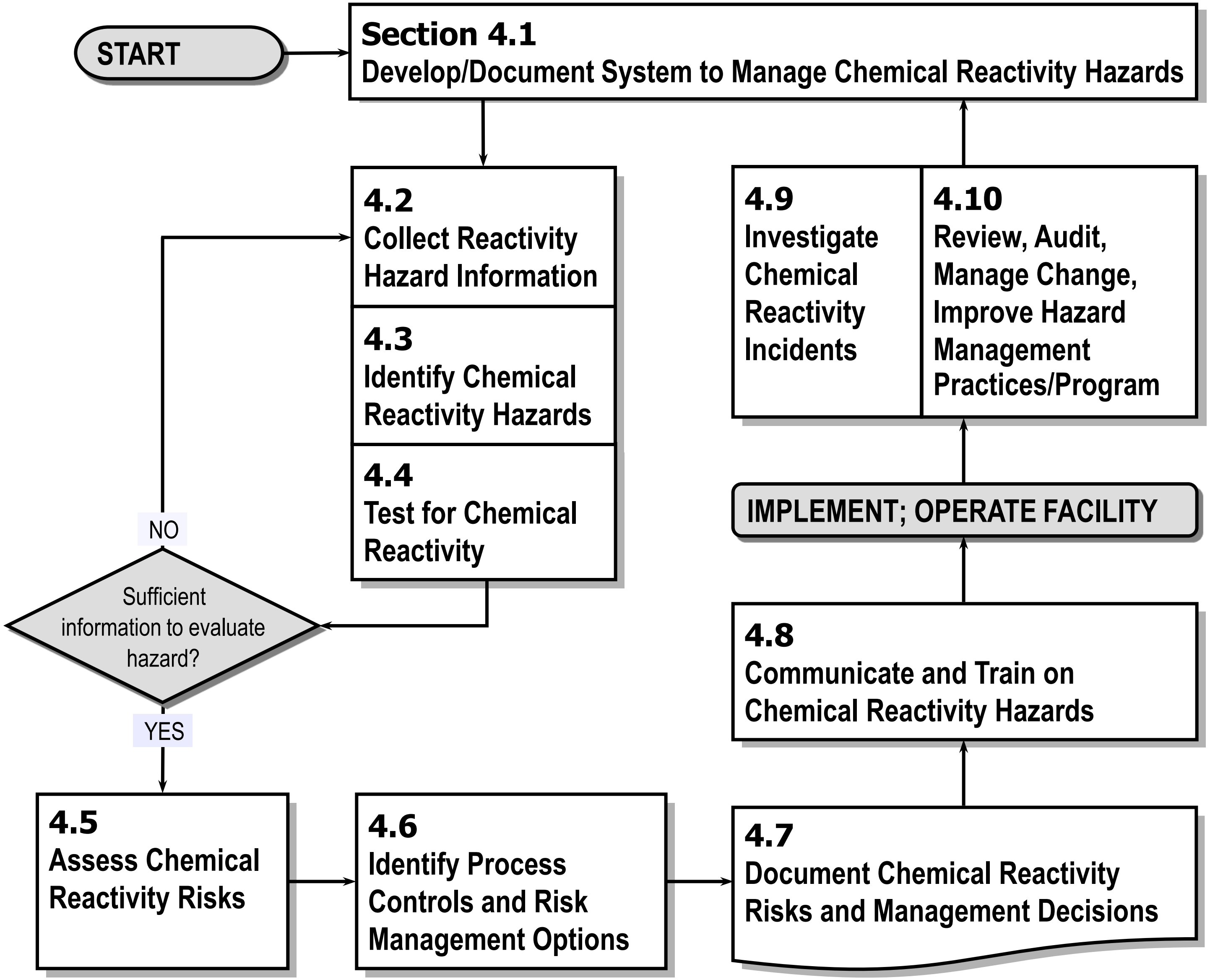


Managing Chemical Reactivity Hazards





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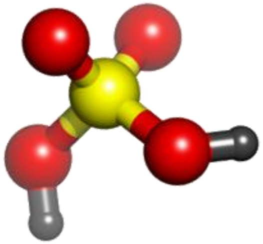
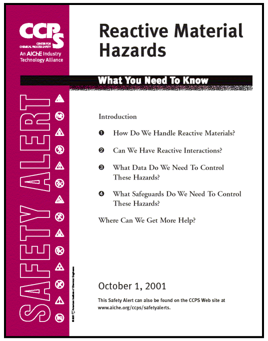


Key steps to avoid unintended chemical reactions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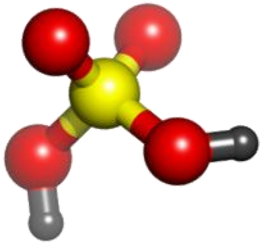
SAFETY ALERT
Reactive Material Hazards
What You Need To Know
Introduction
- How Do We Handle Reactive Materials?
- Can We Have Reactive Interactions?
- What Data Do We Need To Control These Hazards?
- What Safeguards Do We Need To Control These Hazards?

Where Can We Get More Help?

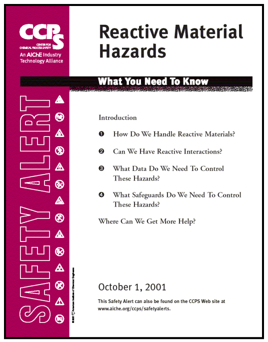
October 1, 2001

This Safety Alert can also be found on the CCPS Web site at www.aiche.org/ccps/safetyalerts.

- Train all personnel to be aware of reactivity hazards and incompatibilities and to know maximum storage temperatures and quantities
- Design storage / handling equipment with all compatible materials of construction
- Avoid heating coils, space heaters, and all other heat sources for thermally sensitive materials
- Avoid confinement when possible; otherwise, provide adequate emergency relief protection
- Avoid the possibility of pumping a liquid reactive material against a closed or plugged line
- Locate storage areas away from operating areas in secured / monitored locations



Key steps to avoid unintended chemical reactions (continued)



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SAFETY ALERT

Reactive Material Hazards

What You Need To Know

Introduction
- How Do We Handle Reactive Materials?
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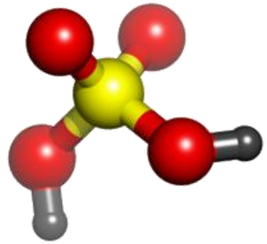
Where Can We Get More Help?

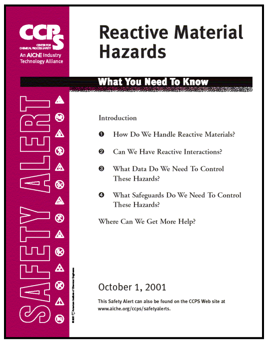
October 1, 2001

This Safety Alert can also be found on the CCPS Web site at www.aiche.org/ccps/safetyalerts.

- Monitor material and building temperatures where feasible with high temperature alarms
- Clearly label and identify all reactive materials, and what must be avoided (e.g., heat, water)
- Positively segregate and separate incompatible materials using dedicated equipment if possible
- Use dedicated fittings and connections to avoid unloading a material into the wrong tank
- Rotate inventories for materials that can degrade or react over time
- Pay close attention to housekeeping and fire prevention around storage/handling areas



Key steps to <u>control intended</u> chemical reactions



- *Scale up very carefully!* – Heat generation increases with the system **volume** (by the <u>cube</u> of the linear dimension), whereas heat removal capability increases with the **surface area** of the system (by the <u>square</u> of the linear dimension).
- Ensure equipment can handle the maximum pressure and maximum adiabatic temperature rise of uncontrolled reactions
- Use gradual-addition processes where feasible
- Operate where the intended reaction will be fast
- Avoid using control of reaction mixture temperature as a means for limiting the reaction rate
- Use multiple temperature sensors in different locations
- Avoid feeding a material above the reactor contents' boiling point

Design safer facilities

The following slides are a summary of D.C. Hendershot, “A Checklist for Inherently Safer Chemical Reaction Process Design and Operation,” *CCPS International Symposium on Risk, Reliability and Security,* New York: AIChE, October 2002

Reaction Hazard Identification

1. Know the heat of reaction for the intended and other potential chemical reactions.
   - You should identify all potential reactions that could occur in the reaction mixture and understand the heat of reaction of these reactions.

Reaction Hazard Identification

2. Calculate the maximum adiabatic temperature rise for the reaction mixture.
   - Use the measured or estimated heat of reaction, assume no heat removal, and that 100% of the reactants actually react.
   - Compare this temperature to the boiling point of the reaction mixture.
   - If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel.

Reaction Hazard Identification

3. Determine the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.
   - This might be done through literature searching, supplier contacts, or experimentation.
   - It will only tell you if any of the individual components of the reaction mixture can decompose at temperatures which are theoretically attainable.

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Reaction Hazard Identification

4. Understand the stability of the reaction mixture at the maximum adiabatic reaction temperature.
   - Are there any chemical reactions, other than the intended reaction, which can occur at the maximum adiabatic reaction temperature?
   - Consider possible decomposition reactions, particularly those that generate gaseous products.
   - Understanding the stability of a mixture of components may require laboratory testing.

Reaction Hazard Identification

5. Determine the heat addition and heat removal capabilities of the pilot plant or production reactor.
   - Don’t forget to consider the reactor agitator as a source of energy – about 2550 Btu/hour/hp.
   - Understand the impact of variation in conditions on heat transfer capability.

Reaction Hazard Identification

6. Identify potential reaction contaminants. In particular, consider possible contaminants that are ubiquitous in a plant environment, such as air, water, rust, oil and grease.
   - Think about possible catalytic effects of trace metal ions such as sodium, calcium, and others commonly present in process water and cleaners.
   - Determine if these materials will catalyze any decomposition or other reactions, either at normal conditions or at the maximum adiabatic reaction temperature.

Reaction Hazard Identification

7. Consider the impact of possible deviations from intended reactant charges and operating conditions.
   - For example, is a double charge of one of the reactants a possible deviation, and, if so, what is the impact?

Reaction Hazard Identification

8. Identify all heat sources connected to the reaction vessel and determine their maximum temperature.
   - Assume all control systems on the reactor heating systems fail to the maximum temperature. If this temperature is higher than the maximum adiabatic reaction temperature, review the stability and reactivity information with respect to the maximum temperature to which the reactor contents could be heated by the vessel heat sources.

Reaction Hazard Identification

9. Determine the minimum temperature to which the reactor cooling sources could cool the reaction mixture.
   - Consider potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material.

Reaction Hazard Identification

10. Consider the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor.
    - Agitation is almost certain to be less effective in a plant reactor, and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature.
    - For exothermic reactions, the temperature may also be higher near the point of introduction of reactants.

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Reaction Hazard Identification

11. Understand the rate of all chemical reactions.
    - It is not necessary to develop complete kinetic models with rate constants and other details, but you should understand how fast reactants are consumed and generally how the rate of reaction increases with temperature.
    - Thermal hazard calorimetry testing can provide useful kinetic data.

Reaction Hazard Identification

12. Consider possible vapor-phase reactions.

These might include:

- combustion reactions
- other vapor-phase reactions such as the reaction of organic vapors with a chlorine atmosphere
- vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

Reaction Hazard Identification

13. Understand the hazards of the products of both intended and unintended reactions.
    - If you find an unexpected material in reaction equipment, determine what it is and what impact it might have on system hazards.
    - For example, in an oxidation reactor, solids were known to be present, but nobody knew what they were. It turned out that the solids were pyrophoric, and they caused a fire in the reactor.

Reaction Hazard Identification

14. Consider doing a Chemical Interaction Matrix and/or a Chemistry Hazard Analysis.
    - These techniques can be applied at any stage in the process life cycle, from early research through an operating plant.

Reaction Process Design

1. Rapid reactions are desirable.
   - In general, you want chemical reactions to occur immediately when the reactants come into contact.
   - The reactants are immediately consumed and the reaction energy quickly released, allowing you to control the reaction by controlling the contact of the reactants.
   - However, you must be certain that the reactor is capable of removing all of the heat and any gaseous products generated by the reaction.

Reaction Process Design

2. Avoid batch processes in which all of the potential chemical energy is present in the system at the start of the reaction step.
   - If you operate this type of process, know the heat of reaction and be confident that the maximum adiabatic temperature and pressure are within the design capabilities of the reactor.

Reaction Process Design

3. Use gradual addition or “semi-batch” processes for exothermic reactions.
   - The inherently safer way to operate exothermic reaction process is to determine a temperature at which the reaction occurs very rapidly. Operate the reaction at this temperature, and feed at least one of the reactants gradually to limit the potential energy contained in the reactor.
   - A physical limit to the possible rate of addition of the limiting reactant is desirable – e.g. a metering pump, small feed line or restriction orifice.

Reaction Process Design

4. Avoid using control of reaction mixture temperature as a means for limiting the reaction rate.
   - If the reaction produces a large amount of heat, this control philosophy is unstable – an increase in temperature will result in faster reaction and even more heat being released, causing a further increase in temperature and more rapid heat release..... If there is a large amount of potential chemical energy from reactive materials, a runaway reaction results.

Reaction Process Design

5. Account for the impact of vessel size on heat generation and heat removal capabilities of a reactor.
   - Heat <u>generation</u> increases with the volume of the system – by the cube of the linear dimension.
   - Heat <u>removal</u> capability increases with the square of the linear dimension.

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Reaction Process Design

6. Use multiple temperature sensors, in different locations in the reactor for rapid exothermic reactions.
   - This is particularly important if the reaction mixture contains solids, is very viscous, or if the reactor has coils or other internal elements which might inhibit good mixing.

Reaction Process Design

7. Avoid feeding a material to a reactor at a higher temperature than the boiling point of the reactor contents.
   - This can cause rapid boiling of the reactor contents and vapor generation.

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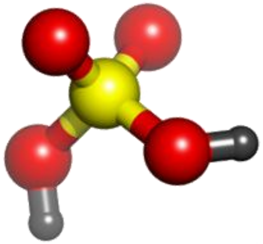


Key Concepts

- Types of reactivity hazards
- Potential consequences
- Runaway reactions
- Contain and control measures
- **Inherently safer systems**

Where chemical reactivity hazard(s) are identified, one of the first questions to ask should be:

"Can the reactivity hazards be eliminated or reduced?"

WHY?

Those hazards that are <u>not</u> eliminated or reduced to insignificance must be managed throughout the lifetime of the facility,

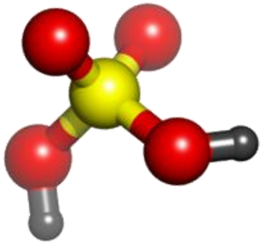
to avoid uncontrolled chemical reactions that can result directly or indirectly in serious harm to people, property or the environment.

Eliminating or reducing
the potential for uncontrolled chemical reactions
makes a facility

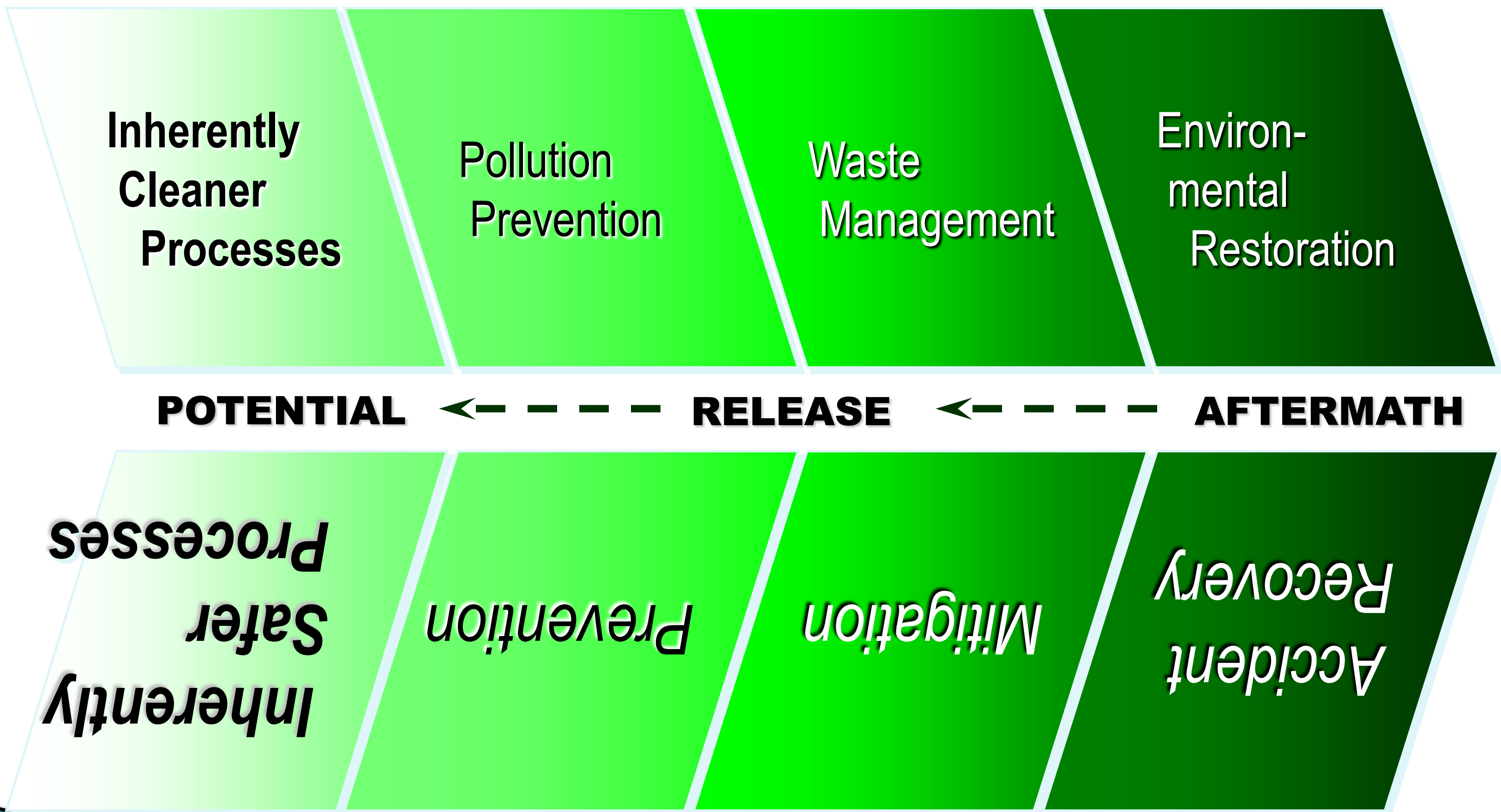
"inherently safer"

If feasible, this has the possibility of affecting a facility in many different ways, such as:

- **Reduce the need for engineered controls and safety systems** (including both initial and ongoing inspection, testing and maintenance costs)
- **Reduce labor costs and potential liabilities associates with ongoing legal compliance**
- **Eliminate the need for personal protective equipment associated with particular hazards**
- **Reduce emergency preparedness and response requirements**
- **Improve worker safety and health**
- **Improve neighborhood / community relations**



Inherently safer processes



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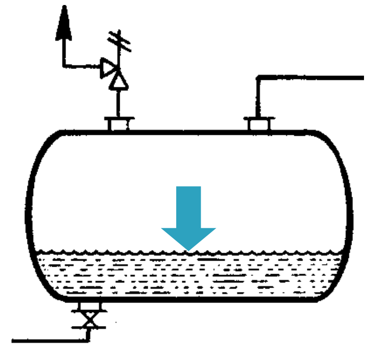
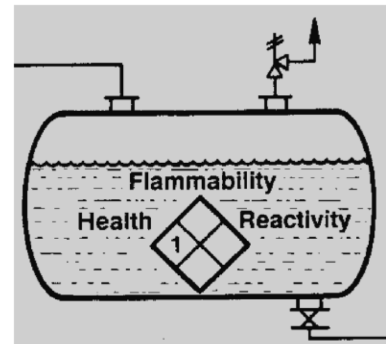
Inherently safer strategies

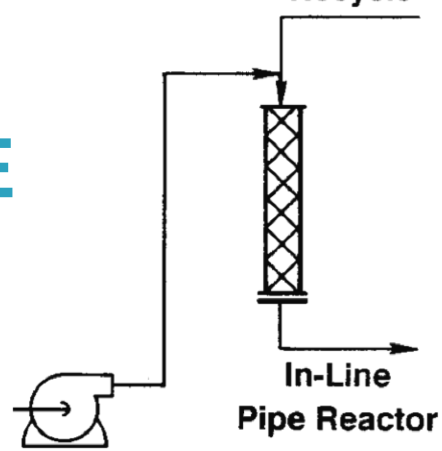
- MINIMIZE



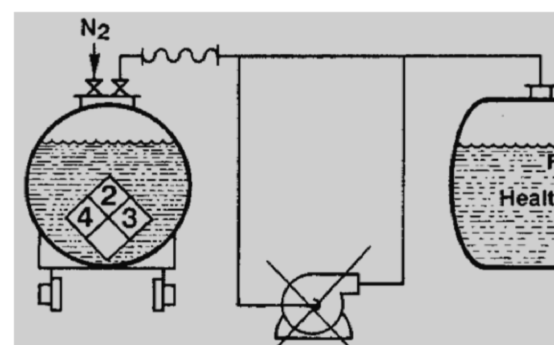
- SUBSTITUTE



- MODERATE



- SIMPLIFY



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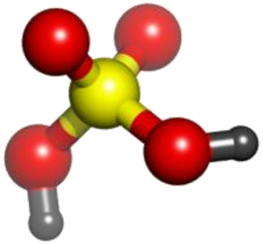
Safe operation

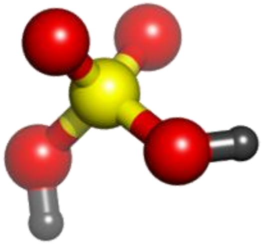
(with respect to chemical reactivity hazards)

- Contain and control all chemical reactivity hazards throughout entire facility lifetime
- ***OR*** **Reduce hazards** or design safeguards such that even if hazard containment or control were lost, no injuries, property damage, environmental damage or business interruption would occur
- ***OR*** **Eliminate chemical reactivity hazards**



Inherently safer systems

Case history:
Methyl isocyanate



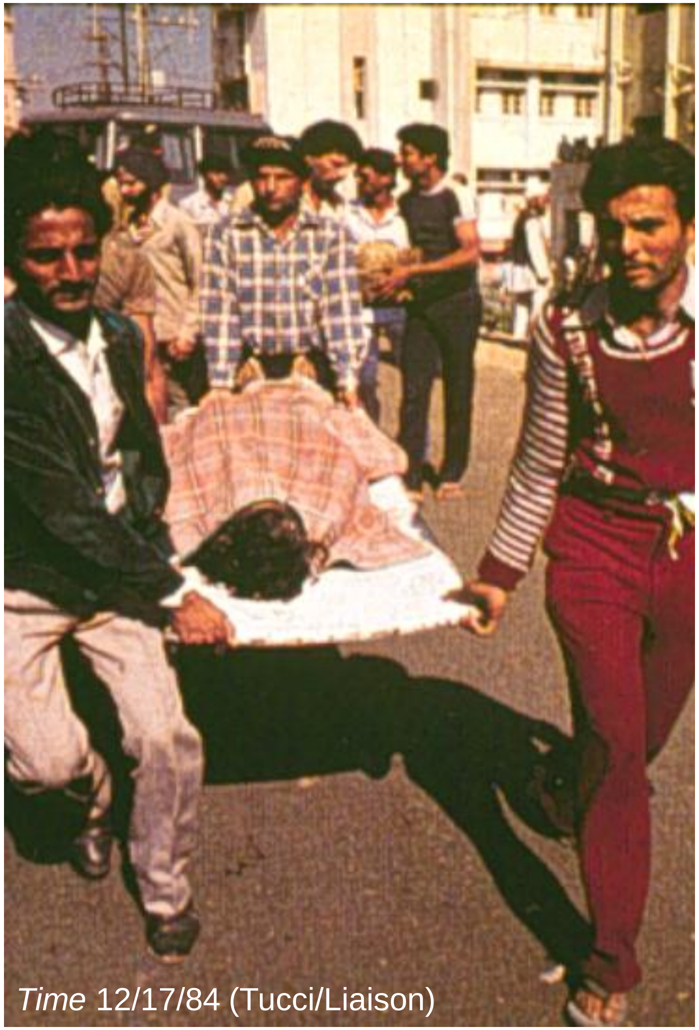
Bhopal

On December 4, 1984, approximately 40 metric tons of methyl isocyanate was released from the UCIL plant in Bhopal, India, resulting in an over 2,000 fatalities and many more injuries.

This was the worst disaster in chemical industry history.

The basic issue:

An uncontrolled chemical reaction occurred, resulting in devastating consequences.

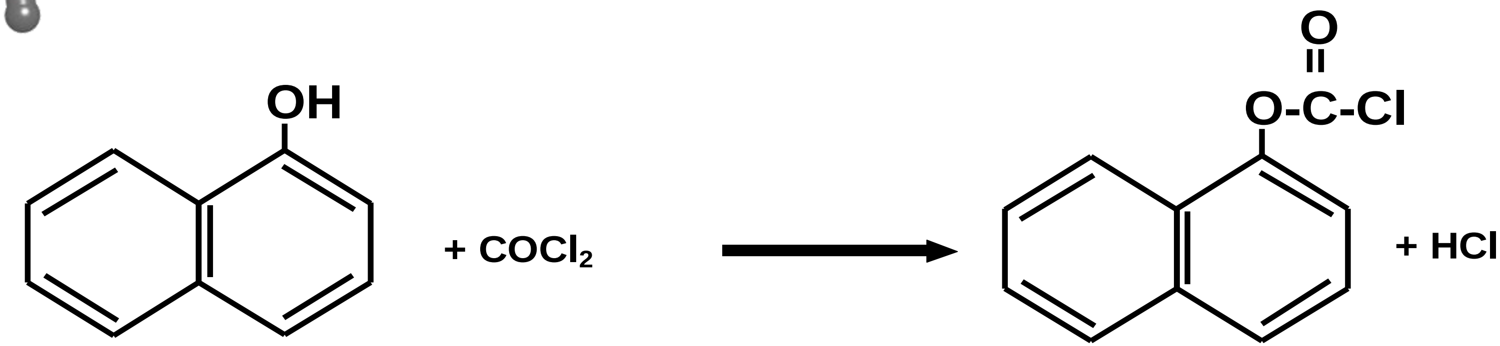


Time 12/17/84 (Tucci/Liaison)

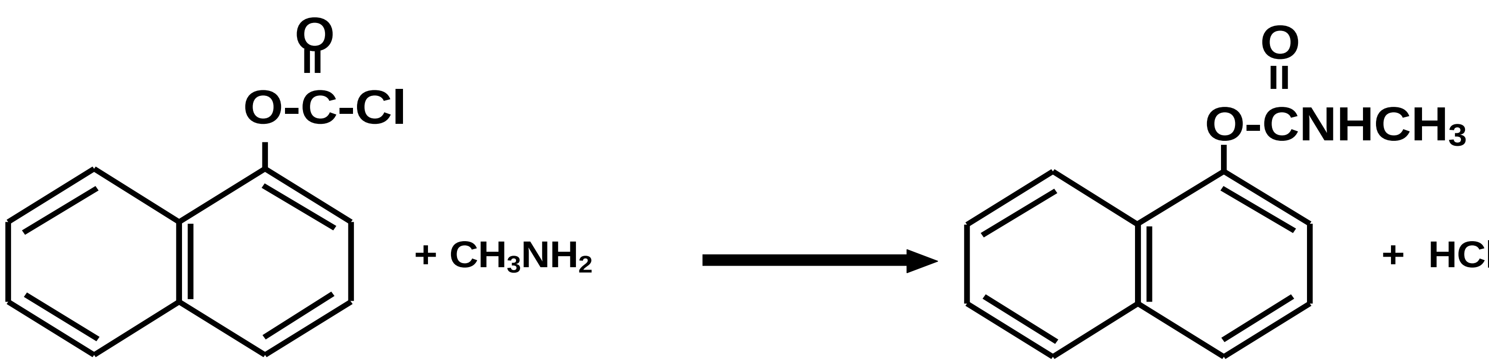
The two theories explaining the Bhopal tragedy both involve a significant amount of water getting into a 15,000 gal (56.5 m3) methyl isocyanate storage tank, resulting in an uncontrolled exothermic reaction that heated the MIC above its boiling point and led to the release of about 40 metric tons (~90,000 lb) of vaporized MIC from an elevated stack.

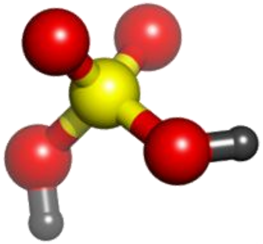
By comparison, the life-threatening concentration of MIC vapors in air is only 5 ppm (ERPG-3, 1 h exposure), which is only about 400 milligrams (~or about 0.001 lb by weight) of MIC in a room about the size of a medium to large bedroom or office (1200 ft3).

Non-MIC route



α- NAPHTHOL CHLOROFORMATE





MIC generated on demand

- One company previously received and stored methyl isocyanate (MIC) in bulk liquefied form, as an ingredient for agricultural chemical products.
- A process modification was made so that the MIC was generated as needed in vapor form, and piped directly to the process that consumed it.

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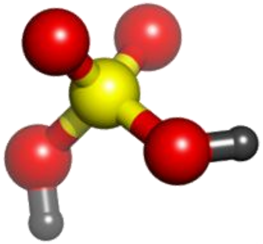

MIC generated on demand

- Average MIC inventory was reduced from thousands of pounds to about 2 pounds (1 kg) of vapor in the transfer line between generation and consumption.
- The possibility of interrupting production (if a problem occurred in the process that generated MIC) was considered to be more than offset by the reduced vapor release risks.

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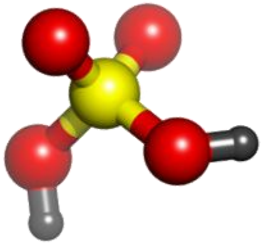
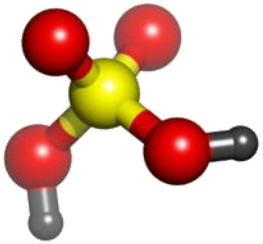


Exercise

What opportunities are there in your field of research or interest to consider reducing chemical reactivity hazards?



Safety and Chemical Engineering Education (SAChE) case histories

- Batch Polystyrene Reactor Runaway
- The Bhopal Disaster
- Methacrylic Acid Tankcar Explosion -video
- Explosion and Fire Caused By a Runaway Decomposition
- Rupture of a Nitroaniline Reactor
- Seveso Accidental Release
- T2 Runaway Reaction and Explosion

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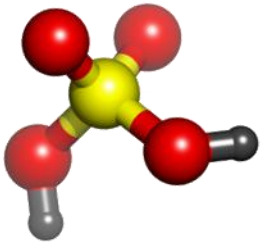


SAChE reactivity modules

Hazards awareness; hazard reduction

- An Introduction to Reactive and Explosive Materials (video)
- Acrylic Monomers Handling
- The Hazards of Hydroxylamine
- Chemical Reactivity Hazards (web-based)
- Introduction to Inherently Safer Design

SAChE reactivity modules

Emergency relief systems

- Design for Over-pressure and Under-pressure Protection
- Unit Operations Laboratory Experiment for Runaway Reactions and Vent Sizing
- Relief System Design for Single- and Two-Phase Flow
- Runaway Reactions -- Experimental Characterization and Vent Sizing
- Compressible and Two-Phase Flow with Applications Including Pressure Relief System Sizing

DIERS Users Group

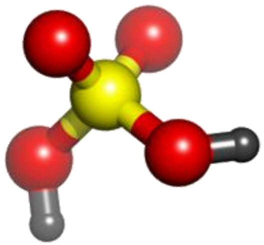
AIChE Design Institute for Emergency Relief Systems

DIERS Users Group Meetings

See www.diers.net/diersweb/home.aspx for schedule and information

Summary

- Aware of the potential consequences of chemical hazards.
- Learned the steps to identifying chemical hazards.
- Learned about the process of reactor design.
- How to contain and control chemical hazards.
- Inherently safer systems were described.



Chemical Waste Management & Disposal

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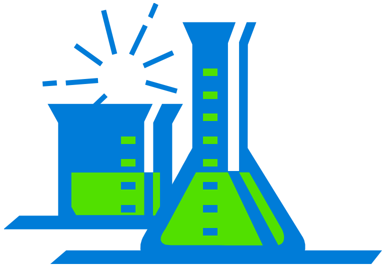
Sandia National Laboratories

Waste Management

- Nonhazardous waste
- General guidelines- Storage – Packaging
- Special categories
  - Metal waste
  - Radioactive and mixed waste
  - Biological waste
  - Unknown and orphan waste
- Treat on-site



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Waste management: nonhazardous waste

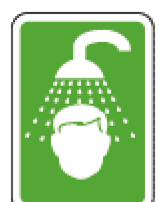
- Used oil (uncontaminated) is not considered hazardous waste. Label Containers "USED OIL", not "hazardous waste"

- Uncontaminated PPE (gloves, wipes)
- Triply rinsed glassware (bottles, droppers, pipettes)
- Salts (KCl, NaCl, Na_2CO_3)

- Sugars - Amino acids
- Inert materials (uncontaminated resins and gels)

Waste management: General guidelines

- Secure and lock waste storage area
- Post signs to warn others
- Keep area well ventilated
- Provide fire extinguishers and alarms, spill kits
- Provide suitable PPE
- Provide eye wash, safety showers
- Do not work alone



Waste management: General guidelines

- Insure against leakage; dyke area if possible
- Label all chemicals, containers, vials
- Separate incompatible chemicals
- Keep gas cylinders separate
- Keep radioactive material separate
- Know how long waste can be stored
- Provide for timely pick-up

Waste - Storage guidance

- Container should not react with the waste being stored (e.g. no hydrofluoric acid in glass)
- Similar wastes may be mixed if they are compatible
- Whenever possible, *wastes from incompatible hazard classes should not be mixed* (e.g. organic solvents with oxidizers)
- Containers must be kept closed except during actual transfers. Do not leave a funnel in a hazardous waste container
- Chemical containers that have been triple-rinsed and air-dried in a ventilated area can be placed in the trash or recycled

Waste – General guidance

- Certain metals cause disposal problems when mixed with flammable liquids or other organic liquids
- Pressure can build up in a waste vessel
- Corrosion can occur in storage vessel
- Secondary containment is necessary
- Glass waste containers can break

Best practice – Orphan control

- Before moving to new job meet with new lab occupant
  - This can be a new employee or new student
  - Label all chemicals and samples carefully
  - Make notations in common lab book
- Dispose of all unneeded or excess chemicals
  - Put into chemical exchange program
  - Dispose of as hazardous waste
- Do not leave any chemicals behind except by agreement

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Waste management

- Recycle, reuse, redistill, if possible
- Dispose by incineration, if possible
- Incineration is NOT the same as open burning

Emissions from incineration vs. open burning

	Open Burn (µg/kg)	Municipal Waste Incinerator (µg/kg)
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2

Source: EPA/600/SR-97/134 March 1998

Laboratory wastes are packaged in small containers

Lab packs consists of small containers of compatible waste, packed in absorbent materials.

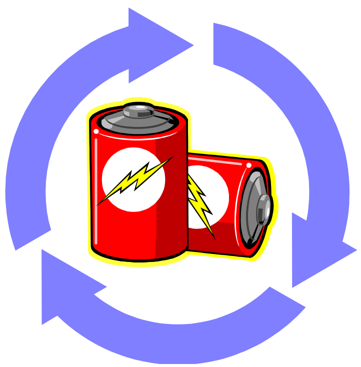
Lab packs segregated at hazardous waste facility

Waste management:
Waste disposal service

- Is disposal service licensed?
- How will waste be transported?
- How will waste be packaged?
- Where will material be disposed?
- How will it be disposed?
- Maintain written records

Battery recycling and disposal

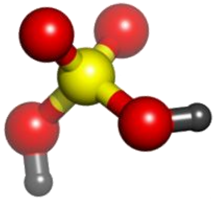
- Hazardous waste
  - Lead acid (Pb) - recycle (90% car batteries)
  - Sealed lead (Pb) – recycle
  - Mercury-oxide (HgO) button, silver-oxide (AgO) button - recycled by jewelers
  - Nickel Cadmium (NiCd) recycle



- Nonhazardous waste
  - Nickel Metal Hydride (Ni-MH) recycle
  - Carbon – zinc
  - Alkaline
  - Zinc-air button

Mercury metal disposal

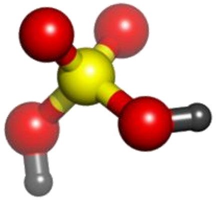
- Collect pure liquid mercury in a sealable container. Label as "MERCURY FOR RECLAMATION"
- Place broken thermometers and mercury debris in a sturdy sealable plastic bag, plastic or glass jar. Label the container "Hazardous Waste - MERCURY SPILL DEBRIS“
- Never use a regular vacuum to clean up a mercury spill - contaminates vacuum, heat evaporates the mercury
- Never use a broom to clean up mercury – spreads smaller beads - contaminates the broom.



Mixed Waste (chemical radioactive)

These wastes must be minimized - heavily regulated

- Universities, hospitals
  - Low level radioactive with chemical
  - Scintillation cocktails
  - Gel electrophoresis waste
- Nuclear energy research
  - Low and high level radioactive with chemical
  - Lead contaminated with radioactivity



Mixed Waste (chemical-biological)

- Medical wastes
  - Blood and tissue
  - Sharps – needles, scalpels
  - Contaminated glassware, PPE
- Autoclave or sterilize
  - Bleach incompatible with autoclave
  - Do not autoclave flammable liquids
- Incinerate

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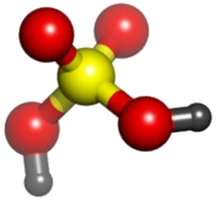

Mixed Waste (radioactive-biological)

- Medical wastes
  - Often disinfect high biohazard to minimize handling risk
  - Let short-lived isotopes decay and then use sanitary sewer
  - Refrigerated storage for putrescible waste (carcasses- tissue)
  - Autoclave or disinfect labware and treat as low level radioactive
  - On-site incineration of low level rad waste if allowed (sharps as well)

Unknown “orphan” waste

Avoid if at all possible -- requires analysis before disposal!

- Pre-screen
  - Crystals present? (potential peroxide formation)
  - Radioactive (Geiger counter)
  - Bio waste? (interview history)

- Screen
  - Prepare for the worst – wear gloves-goggles-hood
    - Air reactivity
    - Water reactivity
    - Flammability
    - Corrosivity

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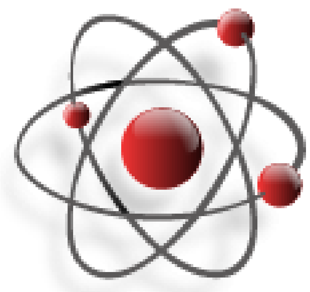
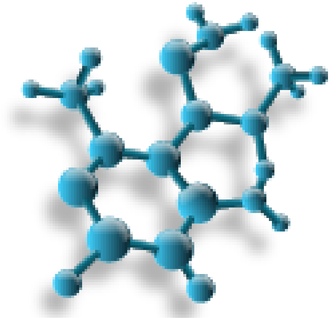
Unknown waste characterization*

- Physical description - Water reactivity - Water solubility
- pH and neutralization information
- Presence of:
  - ✓ Oxidizer
  - ✓ Sulfides or cyanides
  - ✓ Halogens
  - ✓ Radioactive materials
  - ✓ Biohazards
  - ✓ Toxics

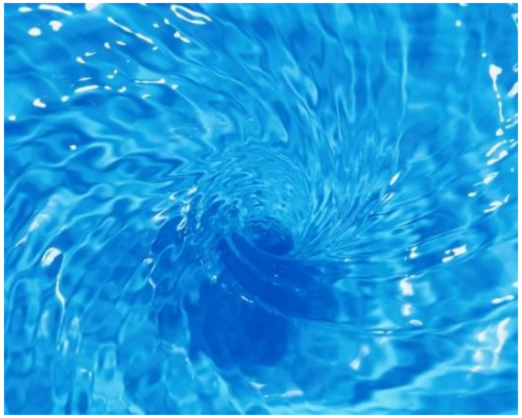


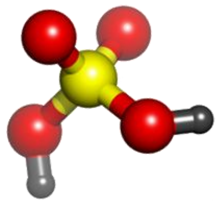


*Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995 Section 7.B.1

Waste management: Down the drain?

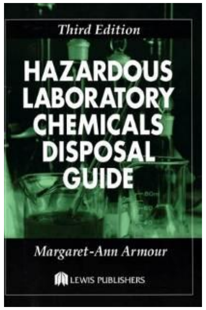
- If legally allowed:
  - Deactivate & neutralize some liquid wastes yourself
    - e.g., acids & bases
    - Don't corrode drain pipes
  - Dilute with lots of water while pouring down the drain
  - Be sure that you do not form more hazardous substances
    - Check reference books, scientific literature, internet

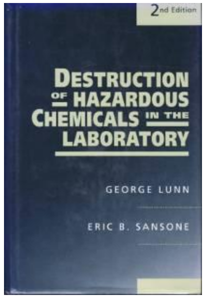


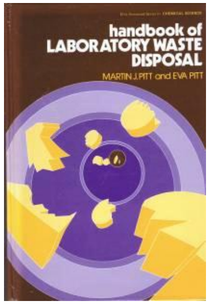


Waste management: Treatment in Lab

- References:
  - "Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 7.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995, available online: http://www.nap.edu/catalog.php?record_id=4911
  - "Destruction of Hazardous Chemicals in the Laboratory, 2nd Edition", George Lunn and Eric B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999.
  - "Hazardous Laboratory Chemicals Disposal Guide, Third Edition", Margaret-Ann Armour, CRC Press, 2003, ISBN 978-1566705677
  - "Handbook of Laboratory Waste Disposal", Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8







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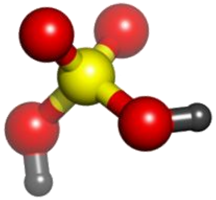

On-site Recycling and Waste Treatment

Waste Management: Recycling

- Recycling by redistribution
- Recycling of metals
  - Gold-mercury-lead- silver
- Recycling of solvents
  - Clean for reuse-rotovap
  - Distill for purity
- Recycling of oil
- Recycling of E-waste

Chemical recycling

Reuse by others in the organization or community

An active chemical exchange program

- Beware of accepting unusable chemicals

Reuse in experiments in the laboratory

Exchange for credit with suppliers by agreement

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What should **not** be recycled

- Gas cylinders past their pressure testing date
- Used disposable pipettes and syringes
- Chemicals and assay kits past their expiration
- Obviously degraded chemicals
- Used tubing, gloves and wipes
- Others?

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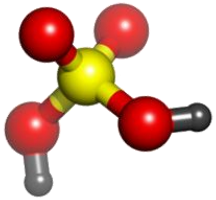
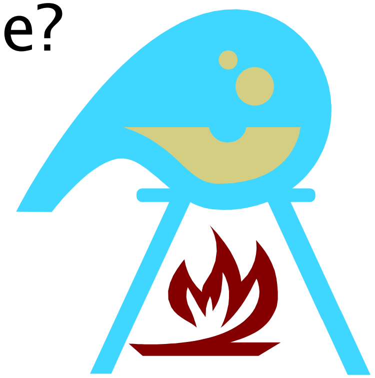


What should be recycled or redistributed?

- Excess unopened chemicals
- Excess laboratory glassware (unused or clean)
- Consumables with no expiration
- Solvent that can be purified
  - Lower purity suitable for secondary use?
- Precious or toxic metals
  - Hg, Ag, Pt, Pd, Au, Os, Ir, Rh, Ru
- Others?



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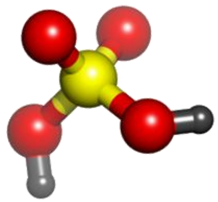
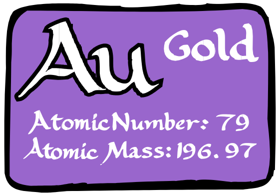
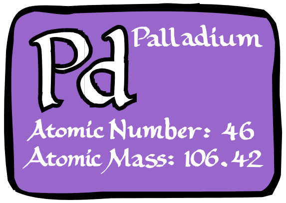


Chemical Recycling – Precious Metal

For reuse in lab or for exchange

- Requires chemical knowledge for lab reuse
- Recover from solution – evaporate then
  - Ignite (Au, Pd, Pt)
  - Reduce with $NaBH_4$ for metal powder or by electroless plating (Pt, Au, Pd, Ag, Rh).
  - Electroplate
  - Metal recovery Ion exchange–then ash





Source : Handbook of Laboratory Waste Disposal, Pitt &Pitt, John Wiley, 1986

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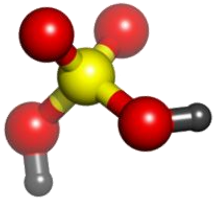

Chemical Recycling – Silver

Recovery from chemical oxygen demand (COD) test
- Acidification and ppt as AgCl

Recovery from photographic fixing solution
- Precipitate as sulfide
- Precipitate with TMT (trimercapto-s-triazine)
- Electrolysis (terminal and in-line)
- Metal replacement (iron containing cartridges)
- Ion exchange

Many companies will buy the recovered silver

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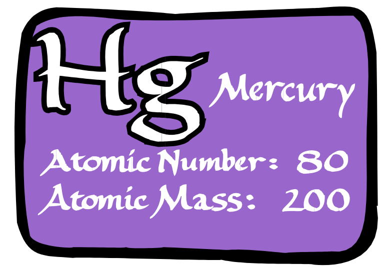
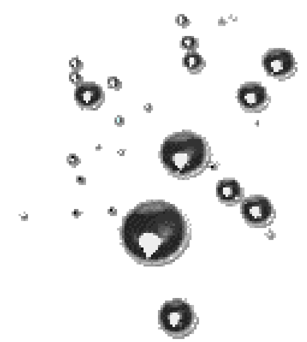
Chemical Recycling – Mercury

- Mercury can be recovered for subsequent lab use or for recycle by vendor
- Remove particulates and moisture by allowing slow drip through a hole in a conical filter paper
- Never distill Hg on-site





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Solvents can be recovered by distillation

- Boiling point must be widely different
- Azeotropes may prevent separation
- Sometimes hazards are created
- Some solvents do not need complete separation
- Hardware for separation

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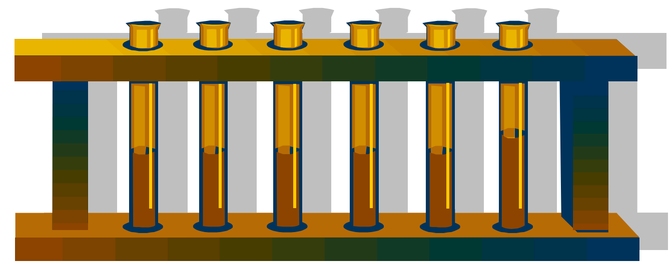
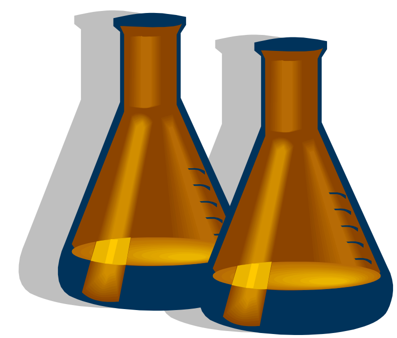
Solvent recycling – general guidance

Solvent recycling requires care and organization

- Keep solvents segregated prior to separation (single product solvent)
- No unnecessary dirt due to careless handling
- Requires good labeling
- A small amount of the wrong chemical can ruin a desired separation
- Care must be taken not to concentrate peroxides





Solvent recycling – general guidance

Solvent recycling requires care and organization

- Try other purification methods before distillation
  - Convert to precipitate
  - Convert to water soluble
  - Use an adsorbent
- Need BP difference of > 10°C
- Can form azeotrope*
  - water / ethanol (100°C/ 78.3°C)
  - cyclohexane / isobutanol (81°C / 108°C)
- Mixture of 4 solvents not practical
- Distillation can be incorporated into curriculum

* Consult CRC Handbook of Chemistry and Physics for list of azeotropes

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Solvent recycling – low efficiency

Rotovap can be used to pretreat

- Toxic material may be kept from the distillation
- May be sufficient if purity is not crucial
- Separation of solvent from solids

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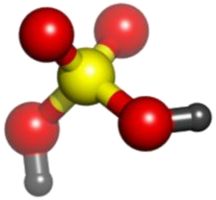
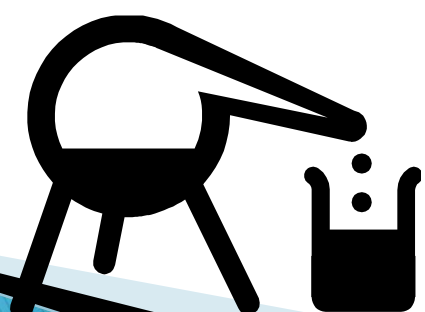


Solvent recycling – medium efficiency

- Even high efficiency stills are not perfect
- Continuous better than batch for large volumes
- Control reflux
- Monitor head temperature
- Reduce heat loss to get more efficiency
- Do not let still operate to dryness
- Use boiling chips but do not add when solvent is hot



Example: 200mm long column for separating benzene and toluene

Packing	TP
Empty	0.5
Coarse packing	1
Fine packing	5

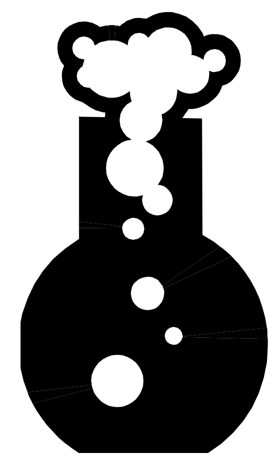
TP = theoretical plates

Solvents that should not be recycled by distillation

Accidents have been reported for these distillations

Individual Substances

- Di-isopropyl ether (isopropyl alcohol)
- Nitromethane
- Tetrahydrofuran
- Vinylidene chloride (1,1 dichloroethylene)

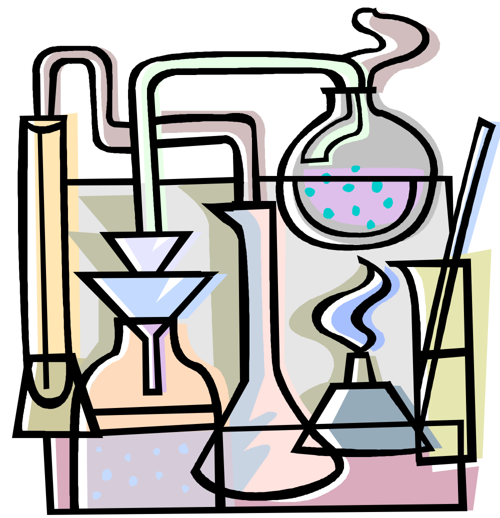


Mixtures

- Chloroform + acetone
- Any ether + any ketone
- Isopropyl alcohol + any ketone
- Any nitro compound + any amine

Practical examples of recycling

- Hexane contaminated with small amount of inert solvent used in prep lab
- Chemistry students given a finite quantity of solvent, then had to recycle for subsequent experiments
- Acetone 50% in water for washing. Azeotrope is 88.5% which is then diluted back with water for reuse
- Use rotovap recovery rather than evaporation. Student will redistill; 60% recovery.
- Third wash was captured and used as first wash on next experiment



Source : Handbook of Laboratory Waste Disposal, 1986.
Marion Pitt and Eva Pitt, John Wiley and Sons, ISBN 85312-634-8

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Solvent recycling

Automated systems help with large needs

HPLC Solvent Recycling

GPC Solvent Recycling

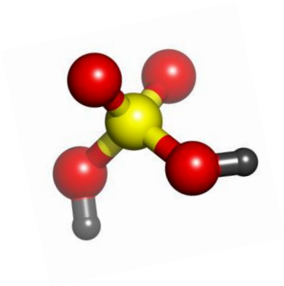
Environmental Laboratory Solvent Recycling

Freon Solvent Recycling

Histology Laboratory Solvent Recycling

General Lab Solvent Recycling Services
Can also be Purchased

Pictures from B/R Instruments: http://www.brinstrument.com/



Tea Break!